

# THÈSE

présentée pour obtenir le grade de

**DOCTEUR DE L'UNIVERSITÉ LOUIS PASTEUR  
DE STRASBOURG**

(DOCTORAT EUROPÉEN)

*DISCIPLINE : CHIMIE PHYSIQUE*

par

**Marc BAADEN**

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**Etudes de molécules extractantes  
en solution et aux interfaces liquide-liquide :  
aspects structuraux et mécanistiques des effets  
de synergie**

**TOME II**

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## Preface × *Preface*

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This is volume 2 of the doctoral thesis. It consists of all color-plates and the supplementary material provided in electronic form on a CD-ROM in the back-cover. The first volume of this thesis contains the main part with text and black and white figures.

The present volume is meant to be used in parallel with volume 1, providing color views and illustrations for chapters 1 to 5. All figures are referred to in the first volume and are numbered continuously for each chapter (*e.g.* 2-5 for the fifth color-plate concerning chapter 2).

For the convenience of the reader, a summary sheet with all abbreviations used in this manuscript is included in volume 1, as well as quick reference cards for the chapters 2 to 5 (Appendix B).





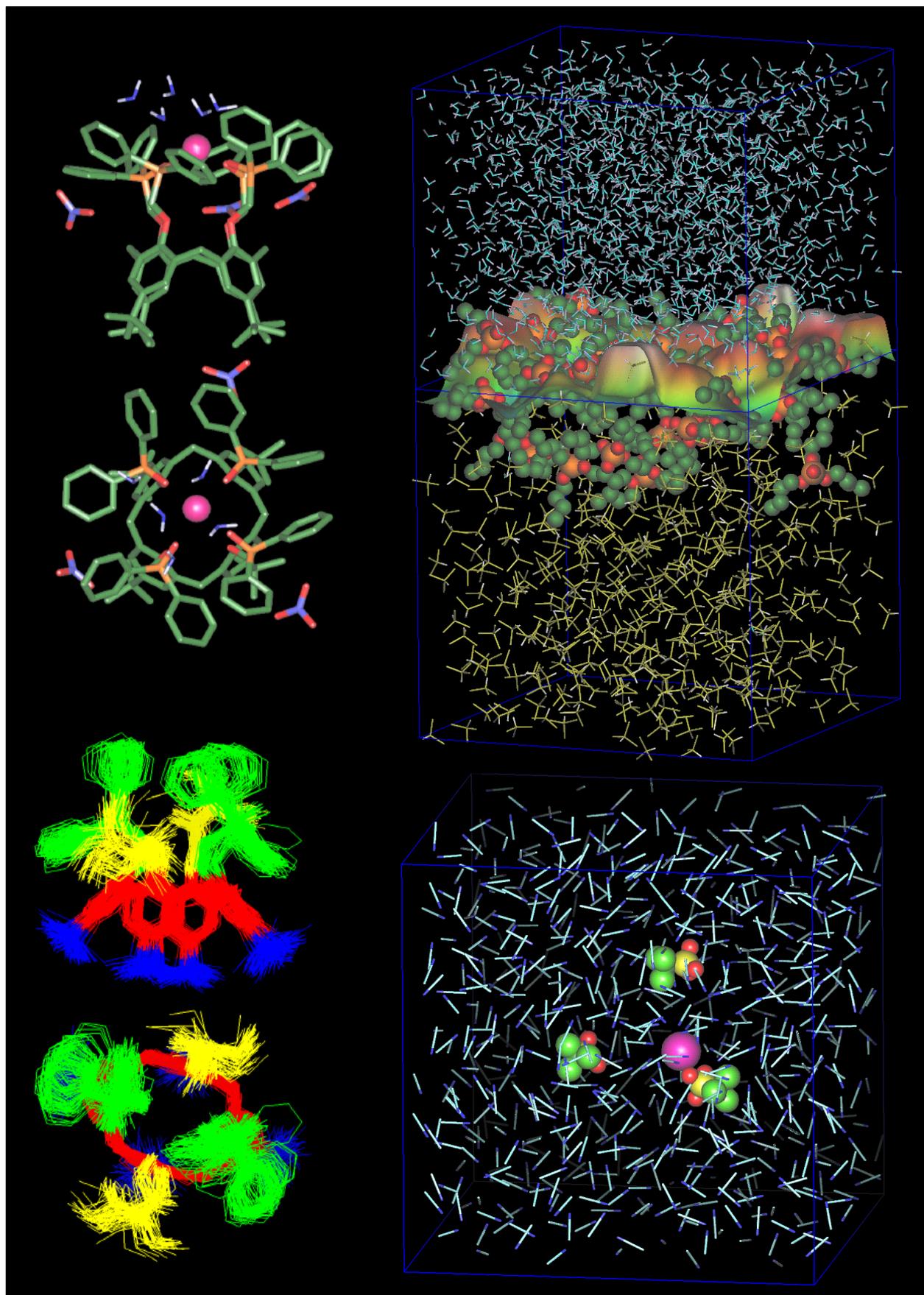


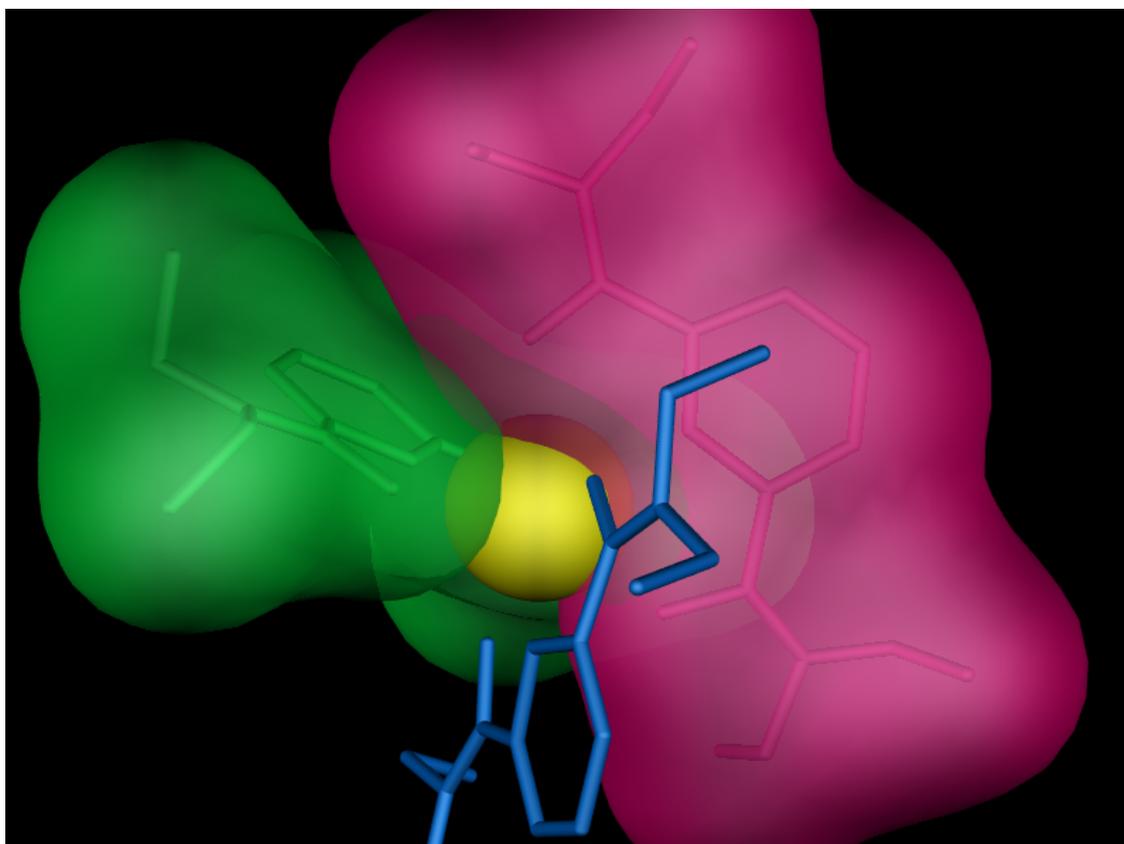
Figure 1-1: Several examples of visualisation results with the MD-DRAW software. On top: orthogonal views of a calixarene with selected solvent molecules (left) and biphasic water/chloroform system (right) with TBP molecules at the interface. The water (blue)/chloroform (yellow) interface is shown. Bottom: cumulated orthogonal views of a calixarene (left) and a  $\text{La}(\text{F}_3\text{CSO}_3)_3$  salt in an acetonitrile simulation box (right).

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# Chapitre 2 × *Chapter 2*

Simulations par DM de la solvataion et de la complexation d'ions lanthanides  $M^{3+}$  par des ligands azotés en solution dans l'acétonitrile: effets du modèle de l'ion, de polarisation du solvant et des contre-ions  
*MD simulations of  $M^{3+}$  lanthanide cation solvation and complexation by N-donor ligands in acetonitrile solution: effects of the cation model, solvent polarization and counterions*

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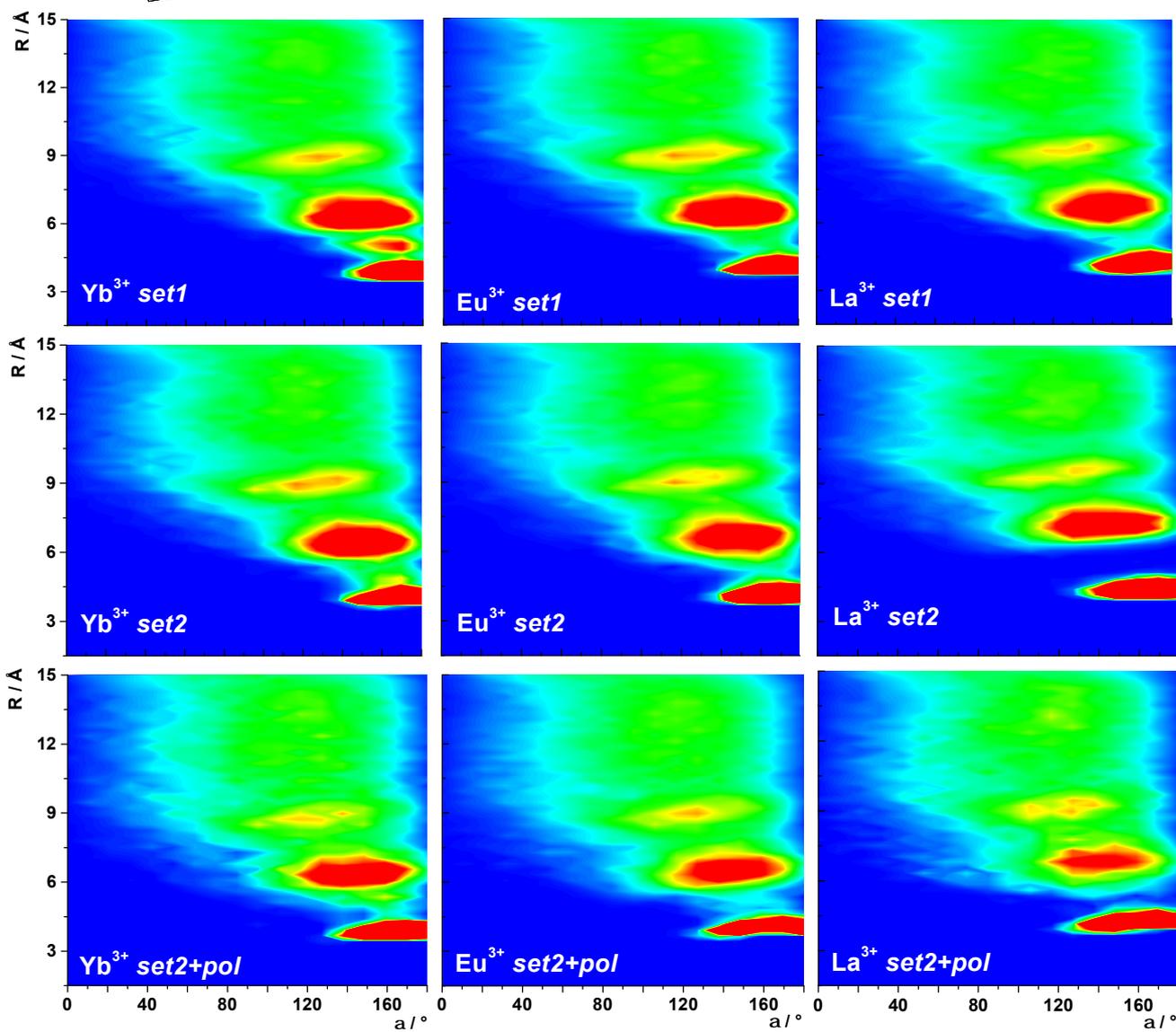
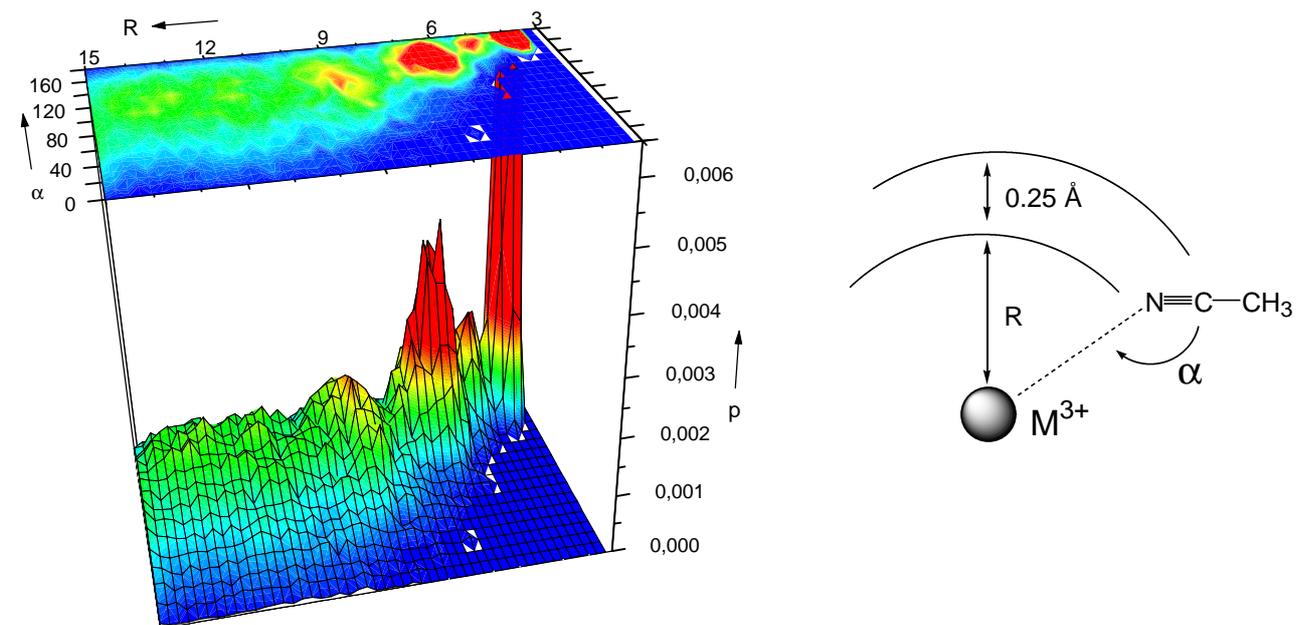


Figure 2-1: Orientation of solvent molecules around  $M^{3+}$  cations in acetonitrile (no counterions): populations of configurations for given ( $R$ ,  $\alpha$ ) values ( $R$  is the distance in Å,  $\alpha$  the angle in degrees). Simulations with set1, set2 and set2+pol. Populations are coded by color, from the minimum (blue) to the maximum (red) value.

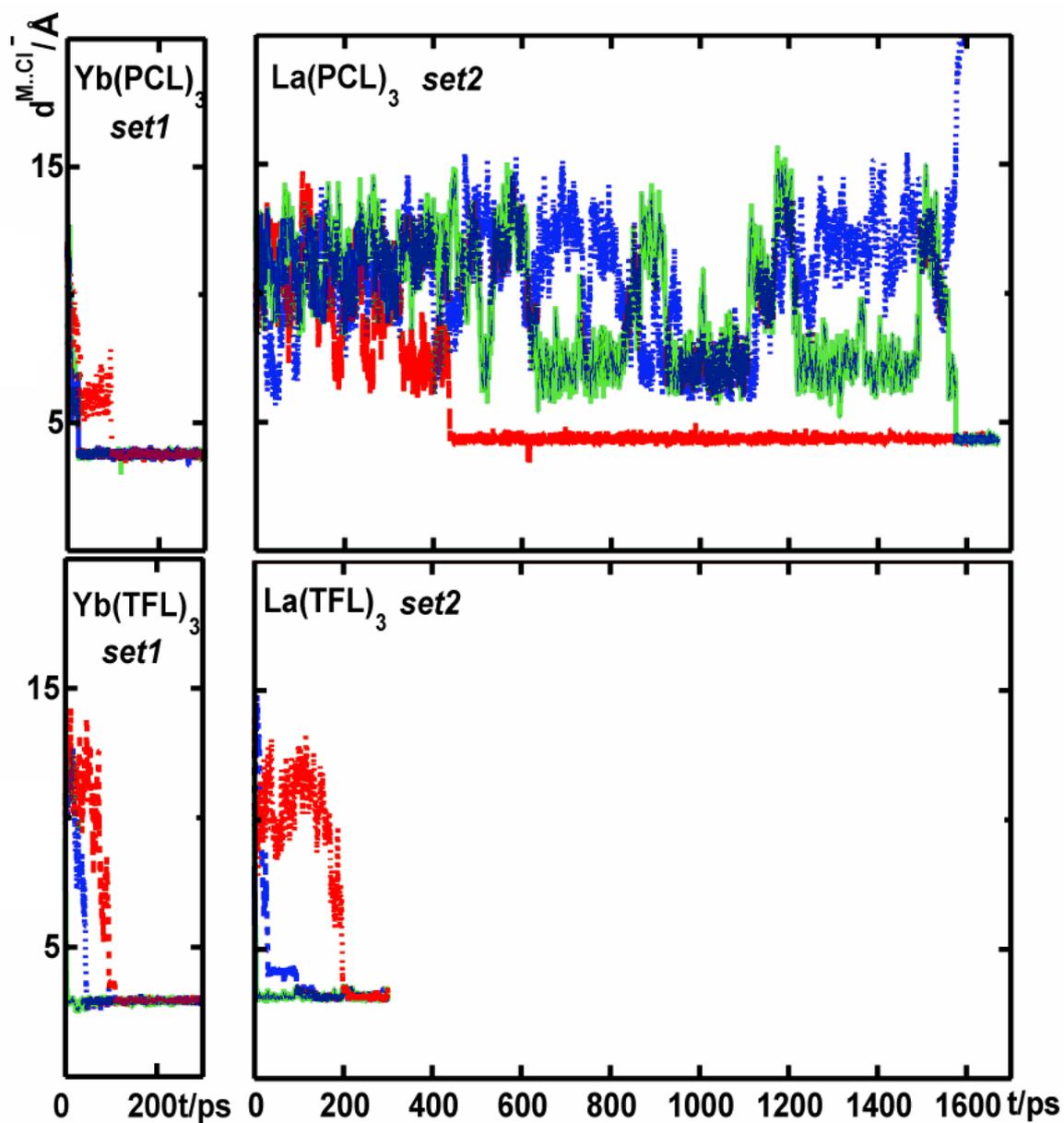


Figure 2-2: Perchlorate (PCL) and triflate (TFL) salts of  $\text{Yb}^{3+}$  (set1) and  $\text{La}^{3+}$  (set2) cations in acetonitrile:  $M^{3+} \cdots X^-$  distances as a function of time (ps). The MD simulations started with fully dissociated ion pairs.

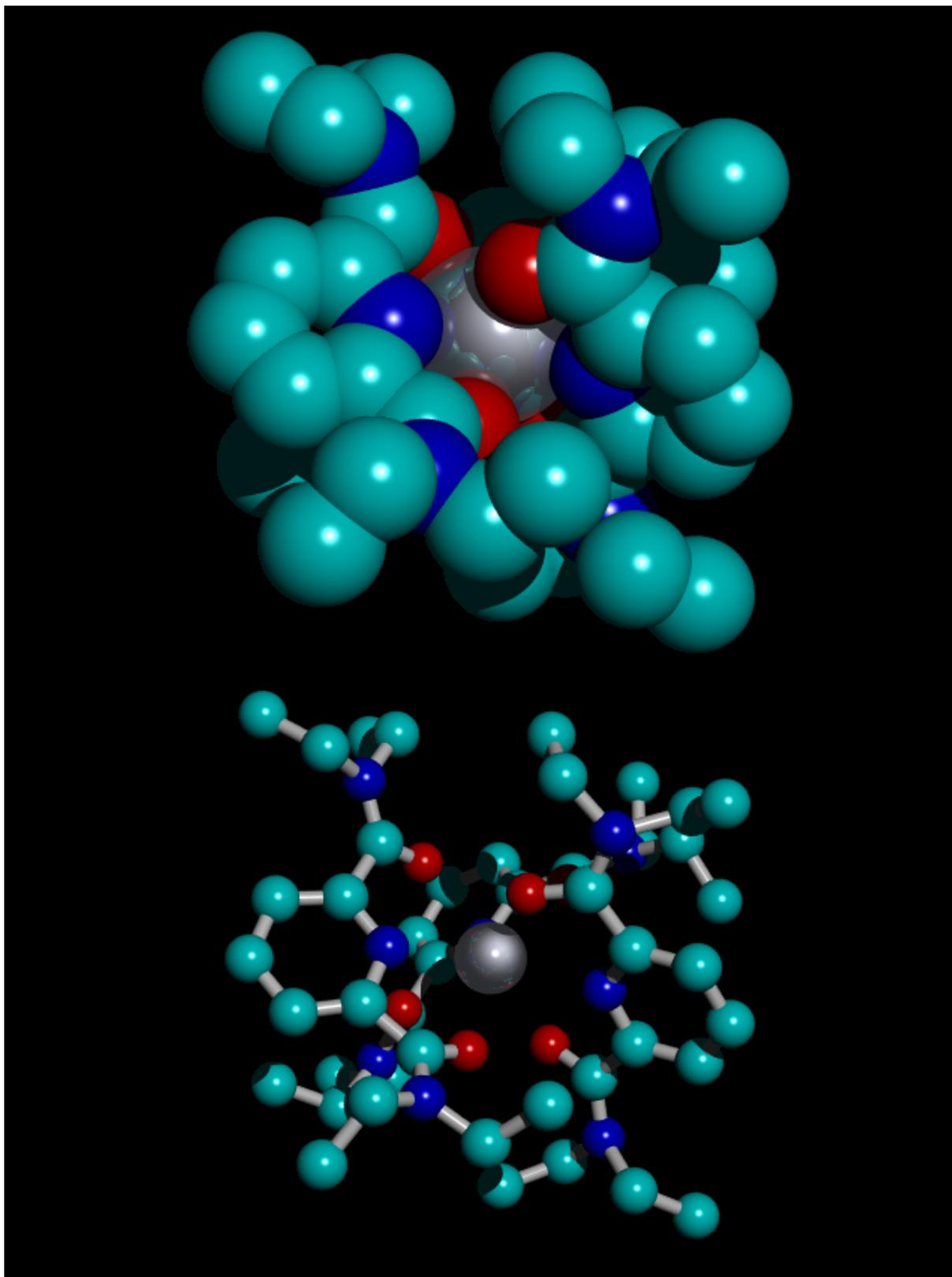


Figure 2-3: Spacefilling (top) and ball-and-stick (bottom) models of the  $\text{EuL1}_3^{3+}$  complex.

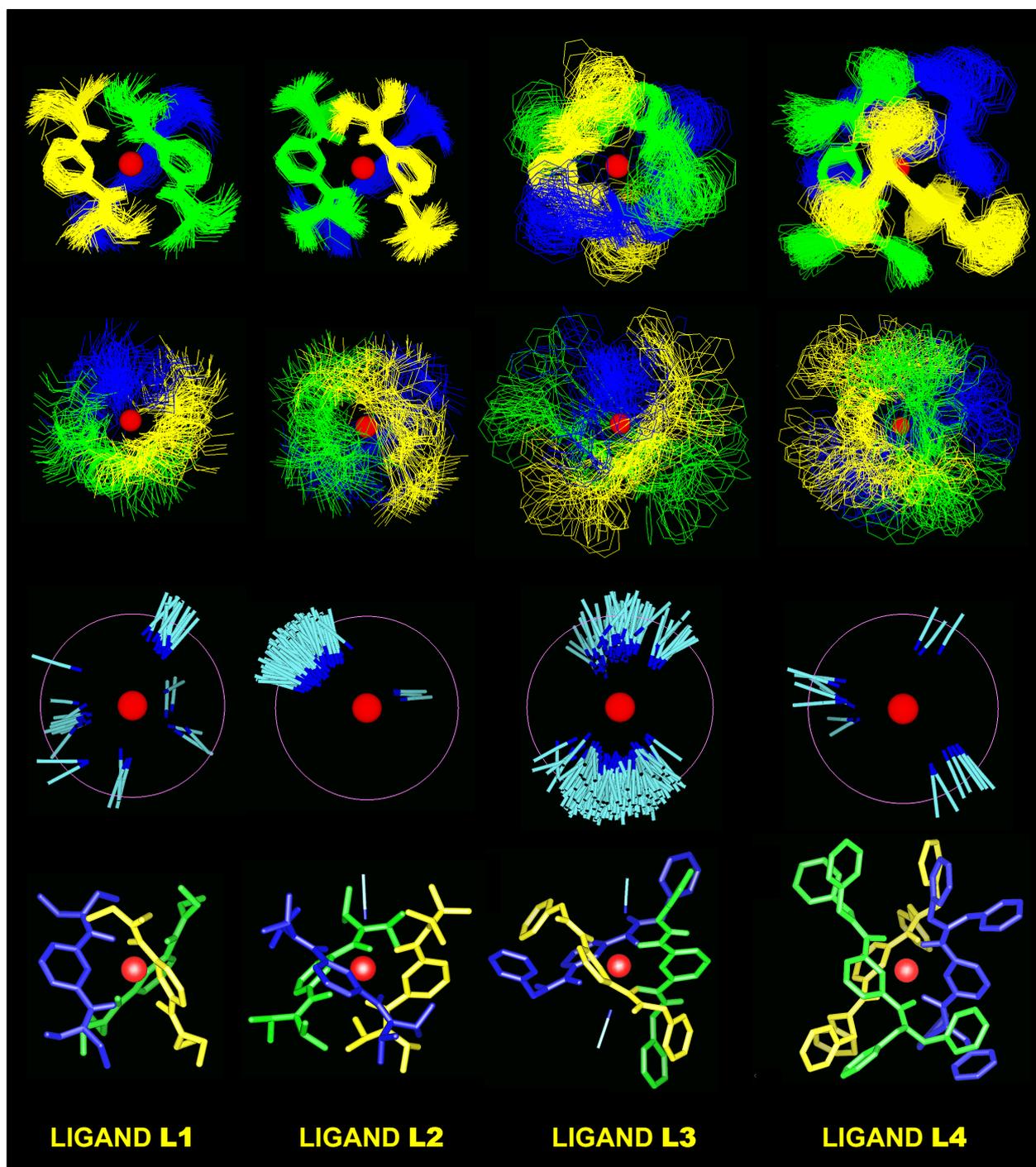


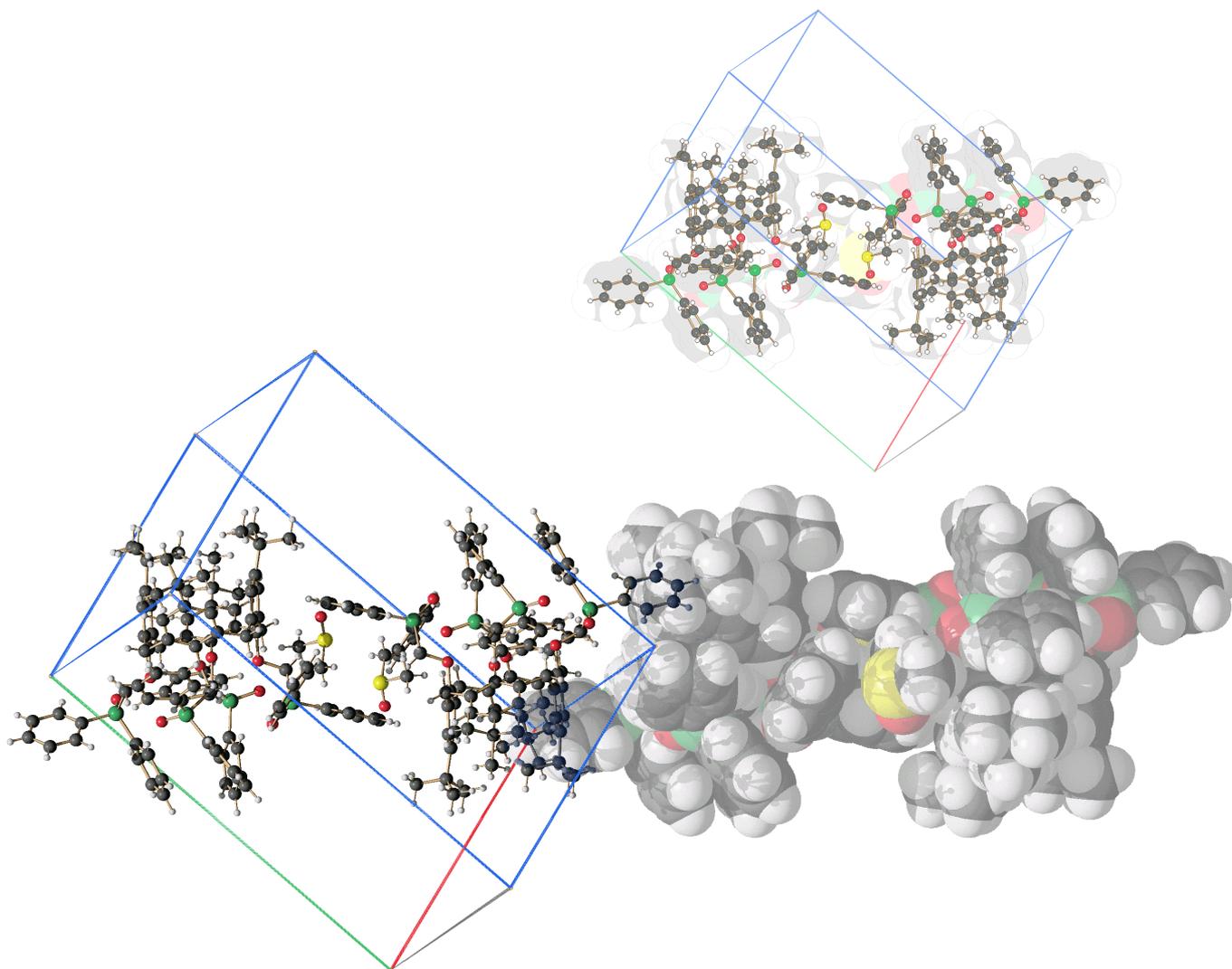
Figure 2-4: Comparison of  $\text{EuL}_3^{3+}$  complexes with  $\text{L}=\text{L1}$  to  $\text{L4}$ . Top row: cumulated views of the complexes in vacuo. Second row: cumulated views of the complexes in acetonitrile solution (solvent molecules are omitted for clarity). Third row: cumulated views of all solvent molecules approaching  $\text{Eu}^{3+}$  closer than 4.5 Å (the ligands are omitted for clarity). Bottom row: snapshots of the complexes with solvent molecules of long lifetime in the solvation shell. All cumulated views were taken over 200 ps at the end of the simulations.

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# Chapitre 3 × Chapter 3

Extraction sélective de terres rares par des dérivés phosphorylés de calix[4]arènes : modélisation et simulations à une interface eau / chloroforme  
*Selective extraction of lanthanide cations by tetra-phosphineoxide substituted calix[4]arenes: a molecular dynamics study at a water / chloroform interface*

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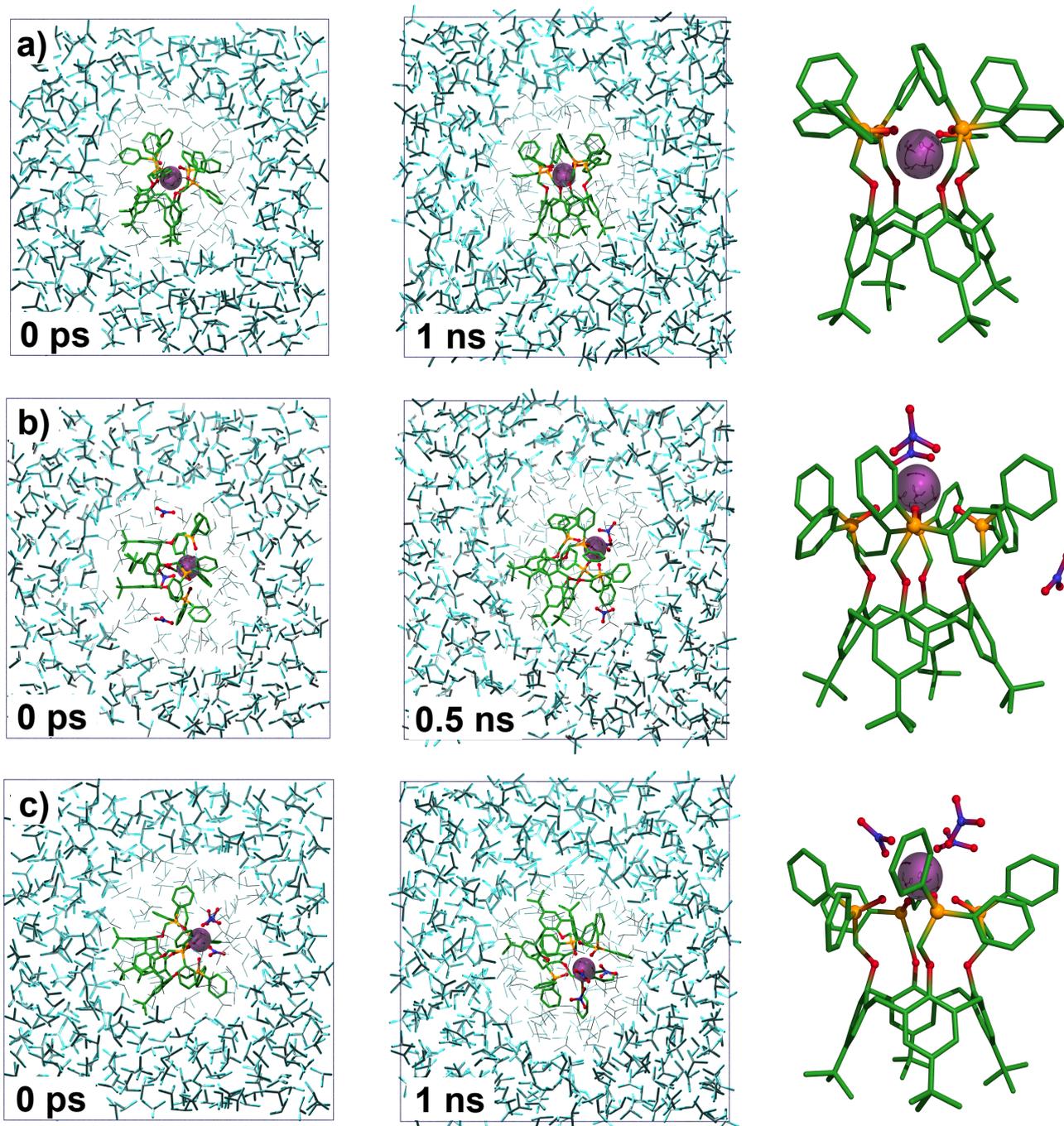


Figure 3-1: a)  $L5Eu^{3+}$  and b), c)  $L5Eu(NO_3)_3$  in "bulk" chloroform. Snapshots of initial (0 ps; left) and final (right) structures. The chloroform molecules around the solute are displayed differently from those of the "bulk" for clarity.

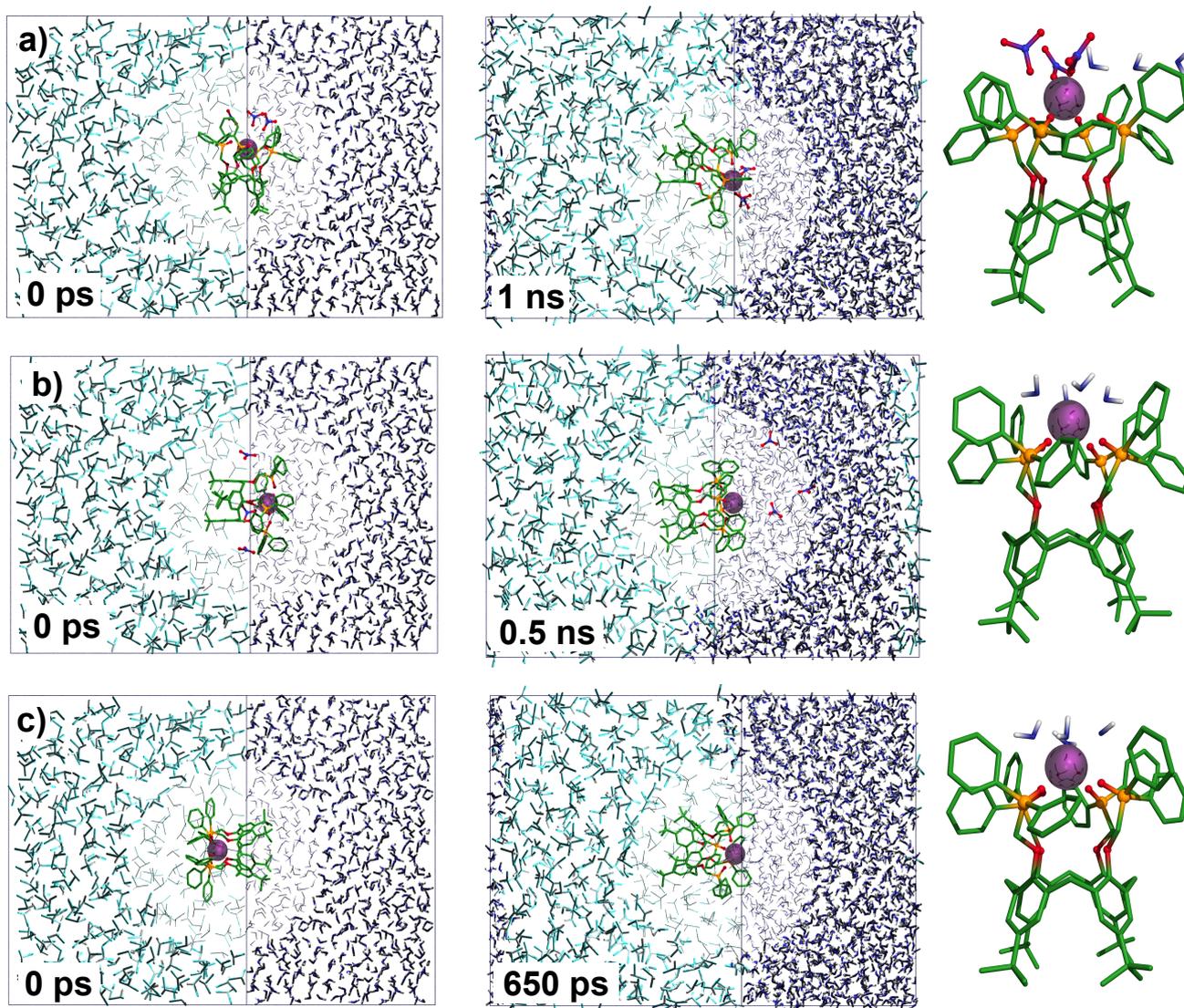


Figure 3-2: a), b)  $L5Eu(NO_3)_3$  and c)  $L5Eu^{3+}$  at the water/chloroform interface. Snapshots of initial (left) and final (right) structures. The solvent molecules around the solute are displayed differently from those of the "bulk" for clarity.

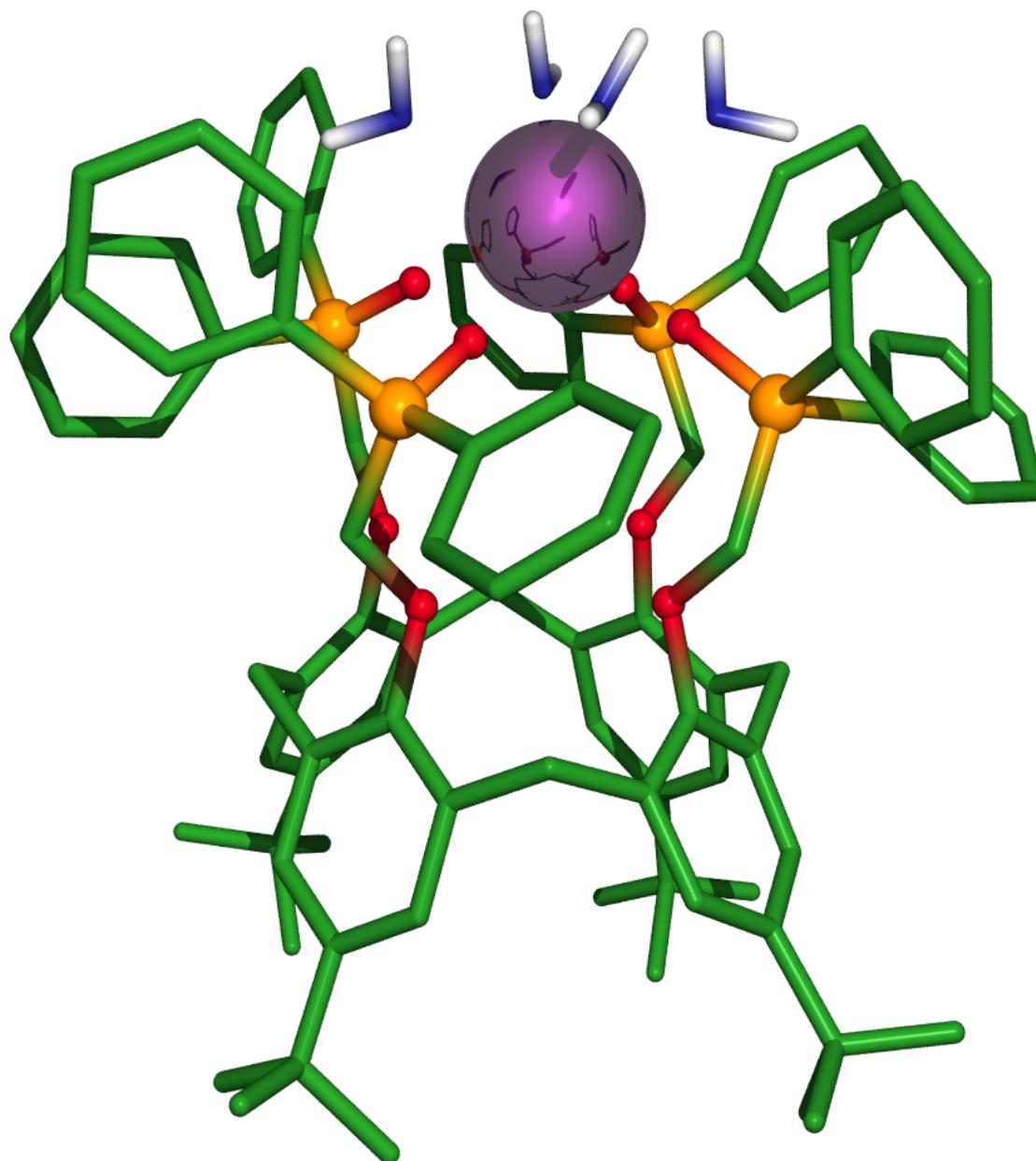
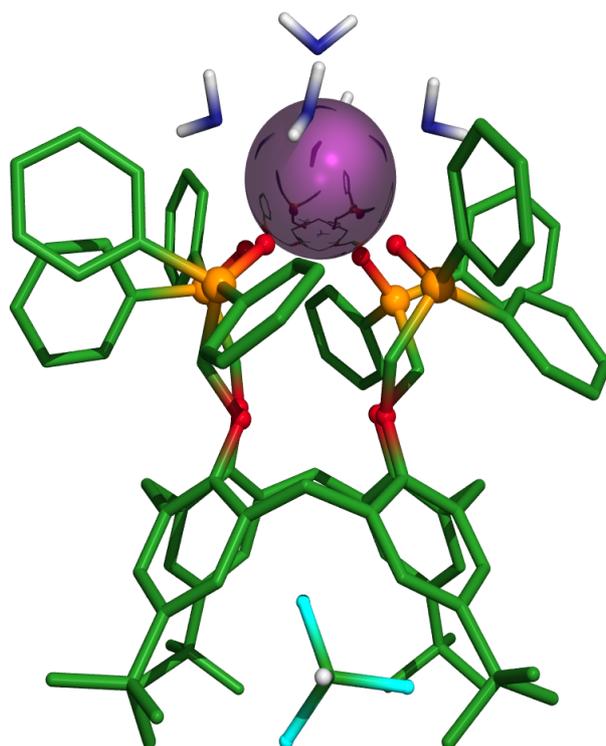
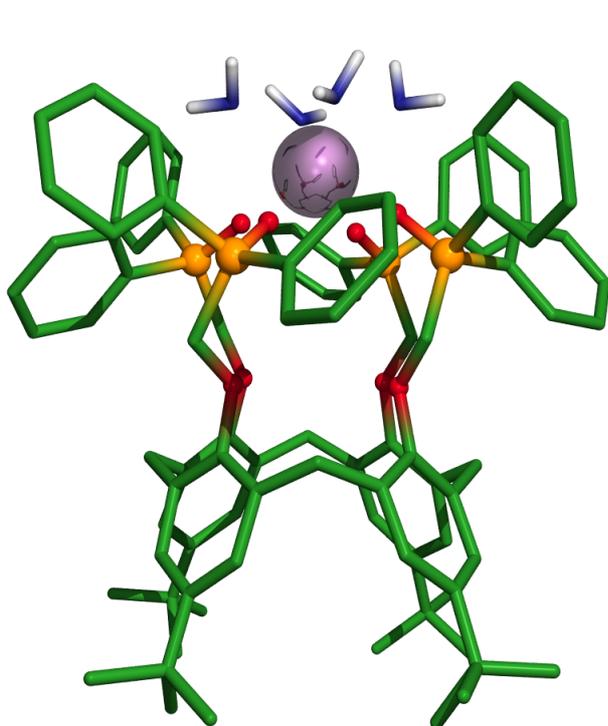


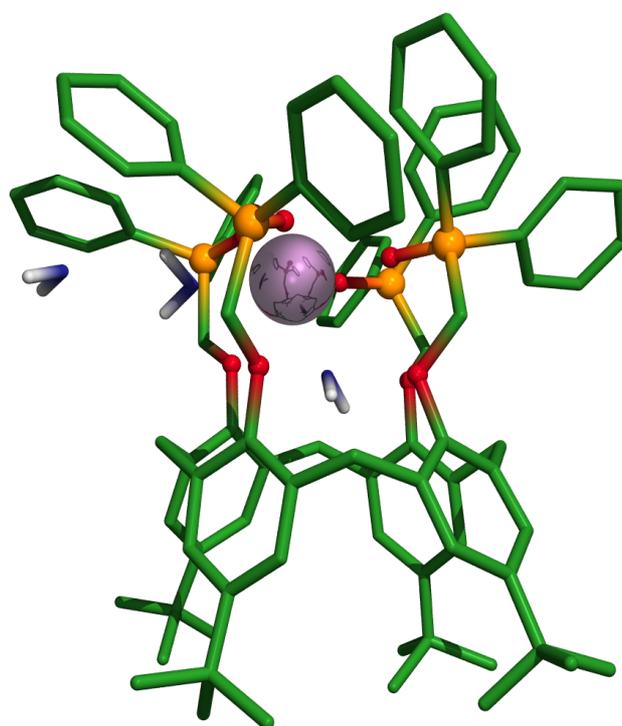
Figure 3-3: A typical view of  $L5Eu^{3+}$  with selected solvent molecules extracted from a simulation at the water/chloroform interface.



a) **L5La<sup>3+</sup>** at 0.7 ns



b) **L5Yb<sup>3+</sup>** at 1 ns



c) **L5Yb<sup>3+</sup>** at 380 ps

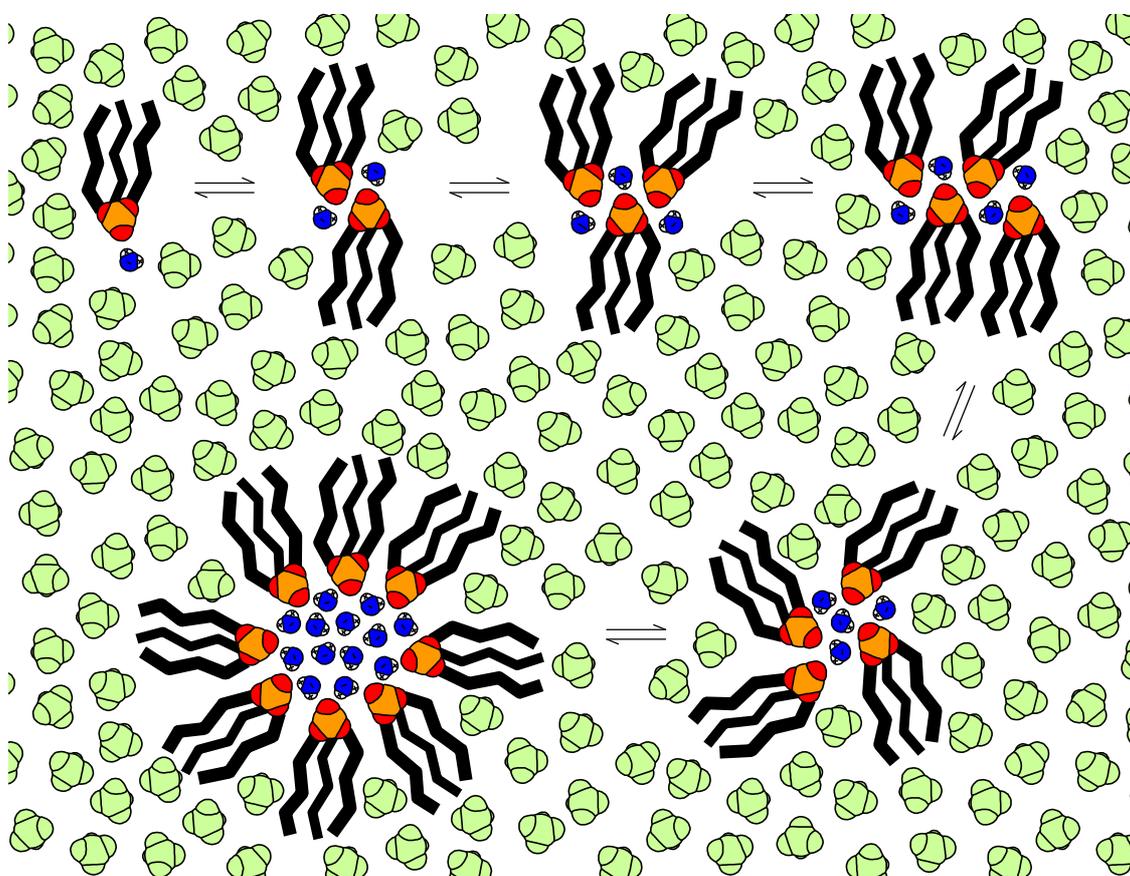
Figure 3-4: a) L5La<sup>3+</sup> and b), c) L5Yb<sup>3+</sup> after MD at a water/chloroform interface. Snapshots of the final structures with selected solvent molecules.

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# Chapitre 4 × Chapter 4

Systèmes complexes comportant des agents de synergie  
et étude du rôle de l'acidité de la phase aqueuse  
*Complex systems with synergists and study of the  
role of aqueous phase acidity*

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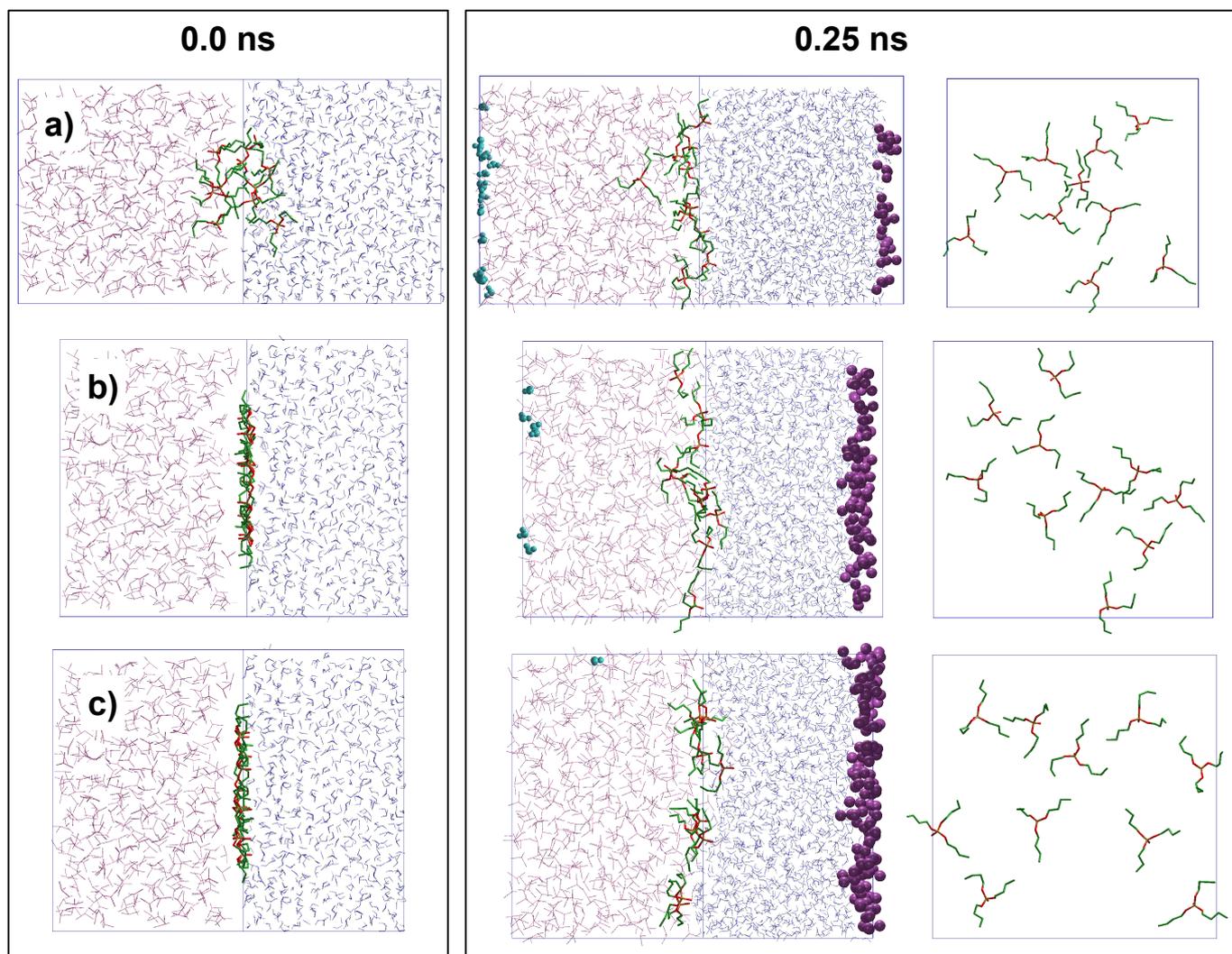


Figure 4-1: Snapshots of the TBP<sub>10</sub> aggregate simulated at the water/chloroform interface (systems **R1** to **R3**). Three starting configurations (left) have been tested: a) bulky arrangement at the interface, b) inverse monolayer with P=O dipoles towards chloroform and c) monolayer with P=O dipoles towards water. Orthogonal views of the final situation are shown on the right, with a spacefilling model for solvent molecules that have crossed the periodic boundary. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface. The trajectories were taken from former work carried out at the MSM laboratory as indicated in the text.

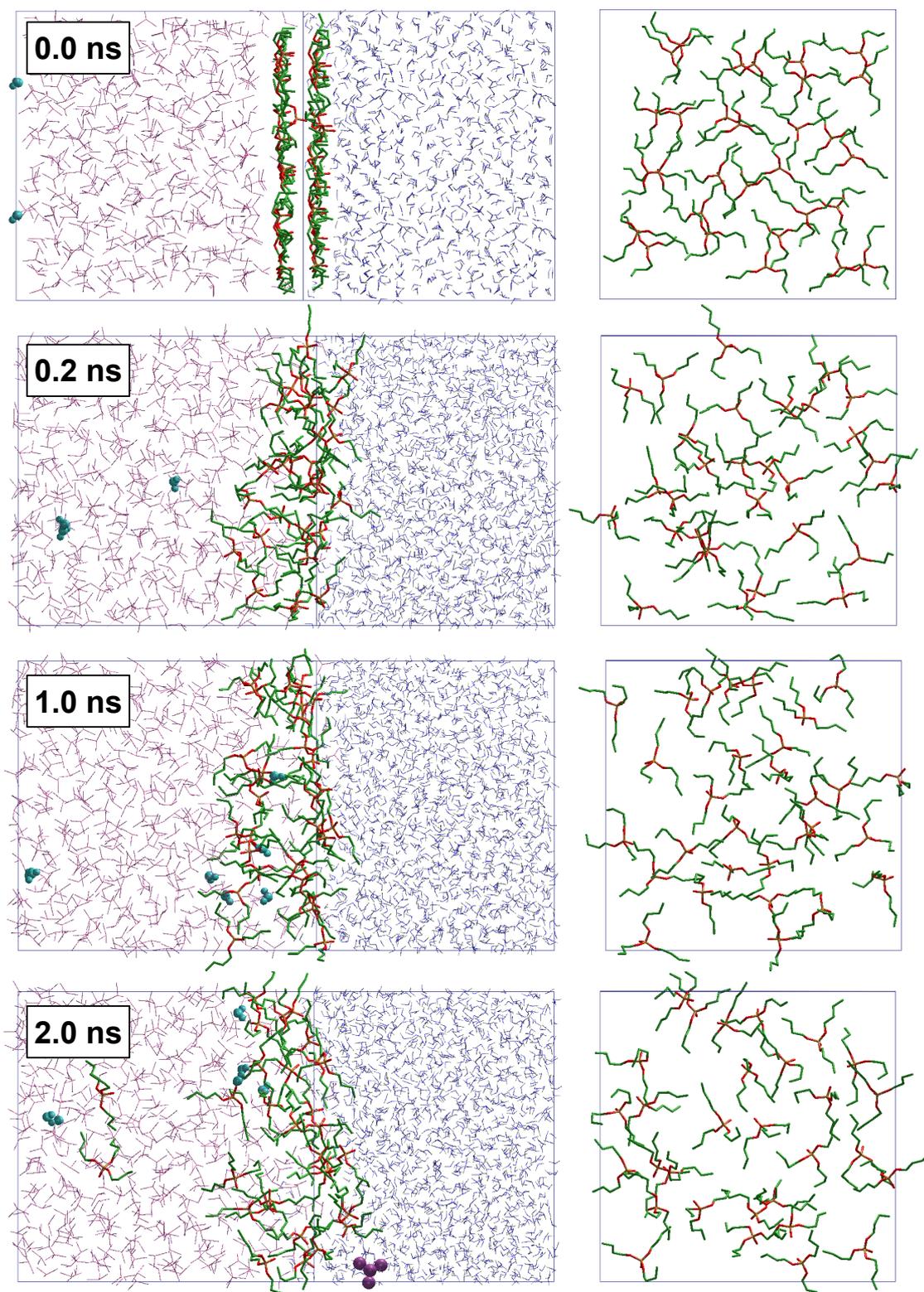


Figure 4-2: Orthogonal views of TBP<sub>30</sub> (system A) simulated at the water/chloroform interface starting from a bilayer with P=O dipoles oriented towards the water phase. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

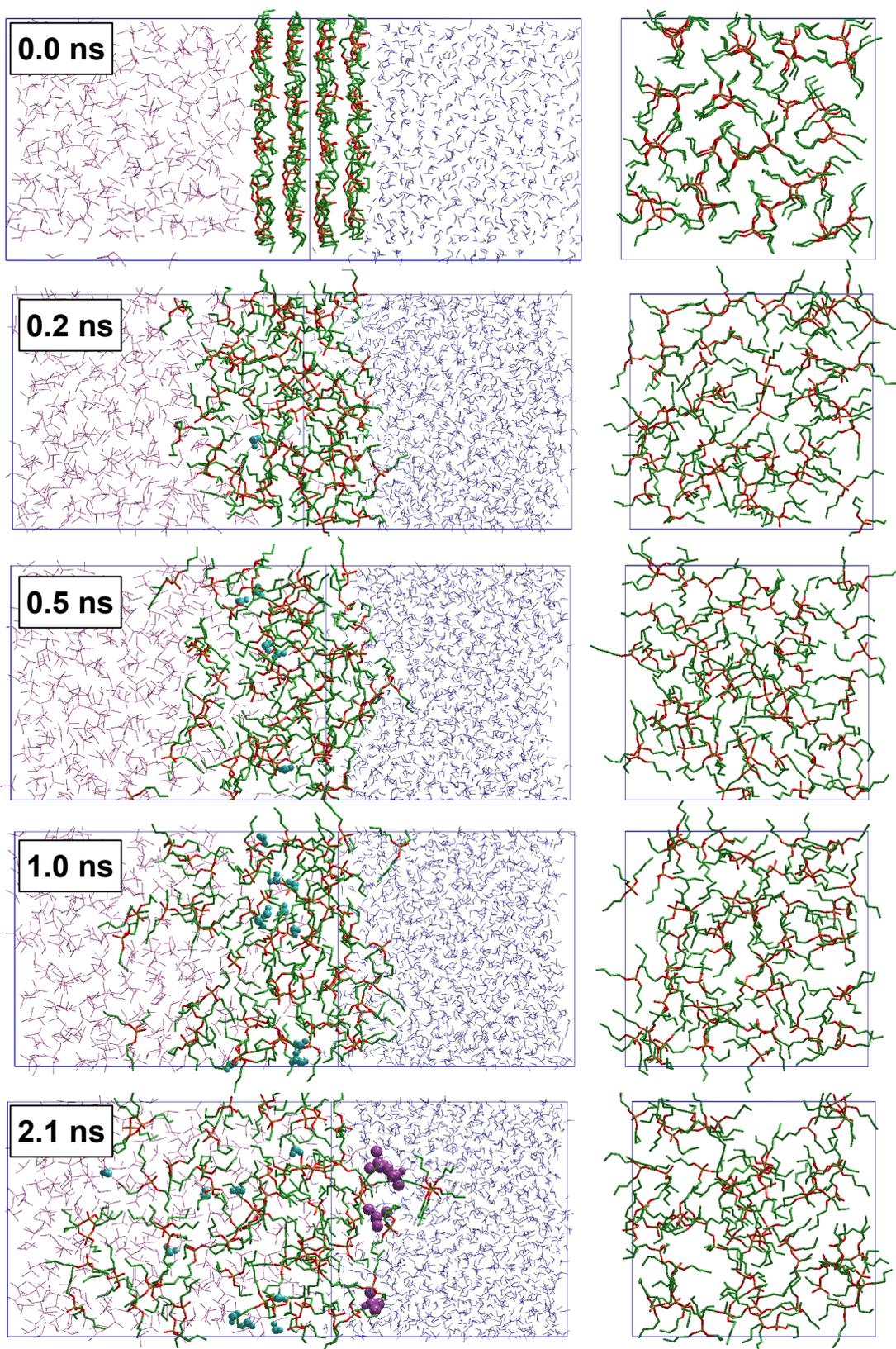


Figure 4-3: Orthogonal views of TBP<sub>60</sub> simulated at the water/chloroform interface starting from a 4-layer configuration with P=O dipoles oriented towards the water phase (system **D1**). Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

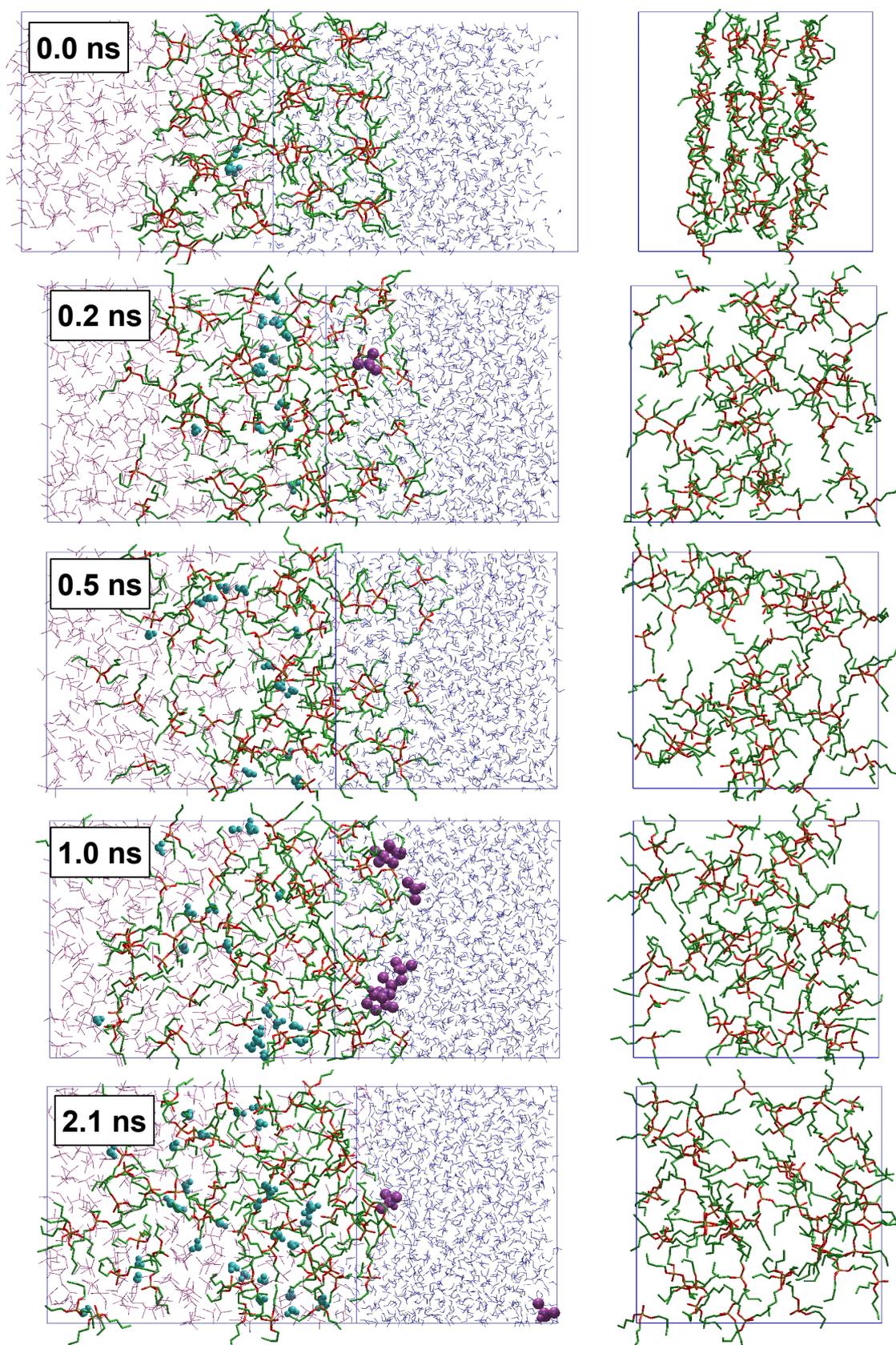


Figure 4-4: Orthogonal views of TBP<sub>60</sub> simulated at the water/chloroform interface starting from a 4-layer configuration perpendicular to the interface (system D2). Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

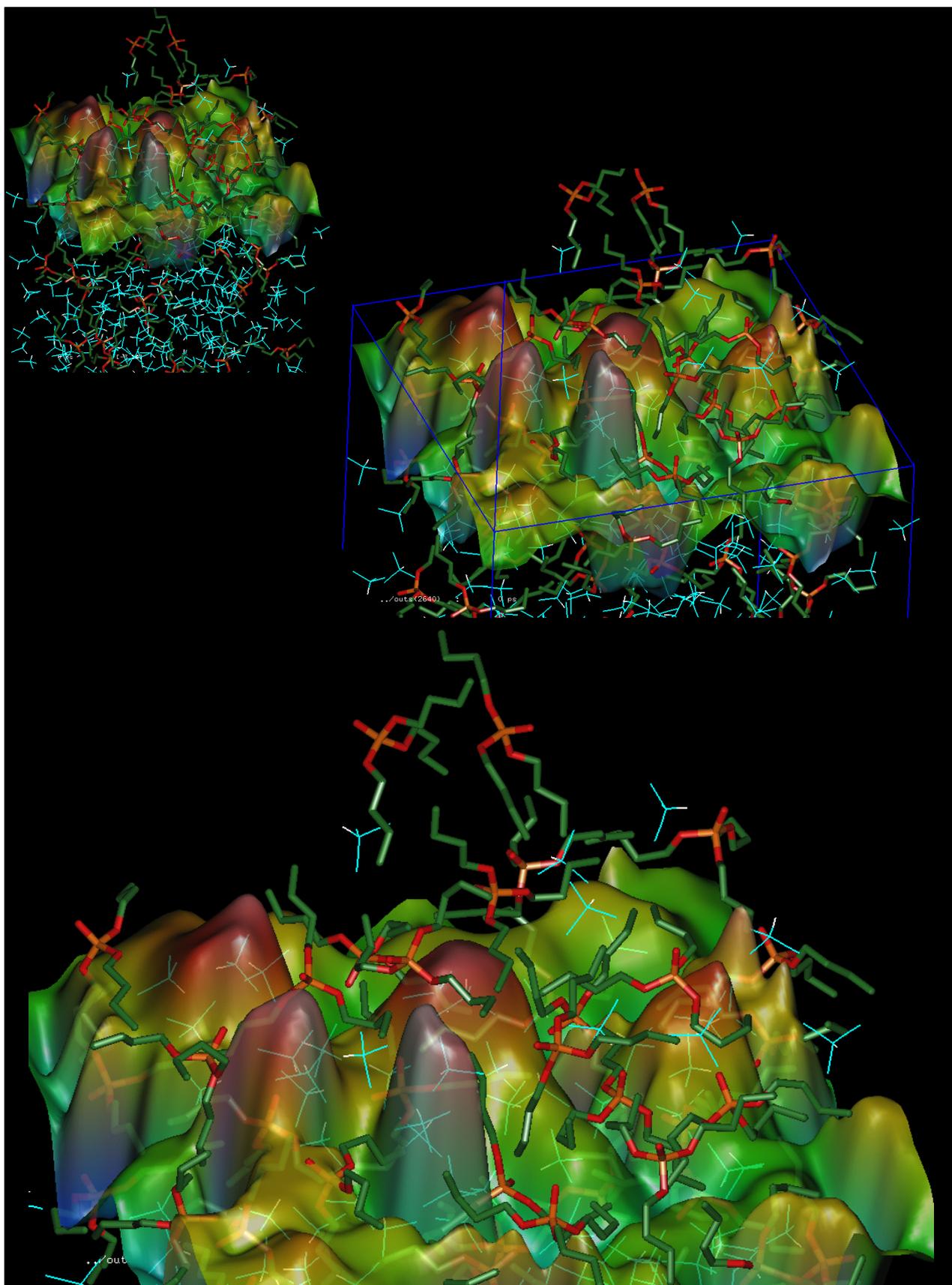


Figure 4-5: Several views of the water/chloroform interface with the TBP<sub>60</sub> system **D1**. The chloroform phase is on the bottom, water on top. The water molecules have been omitted for clarity.

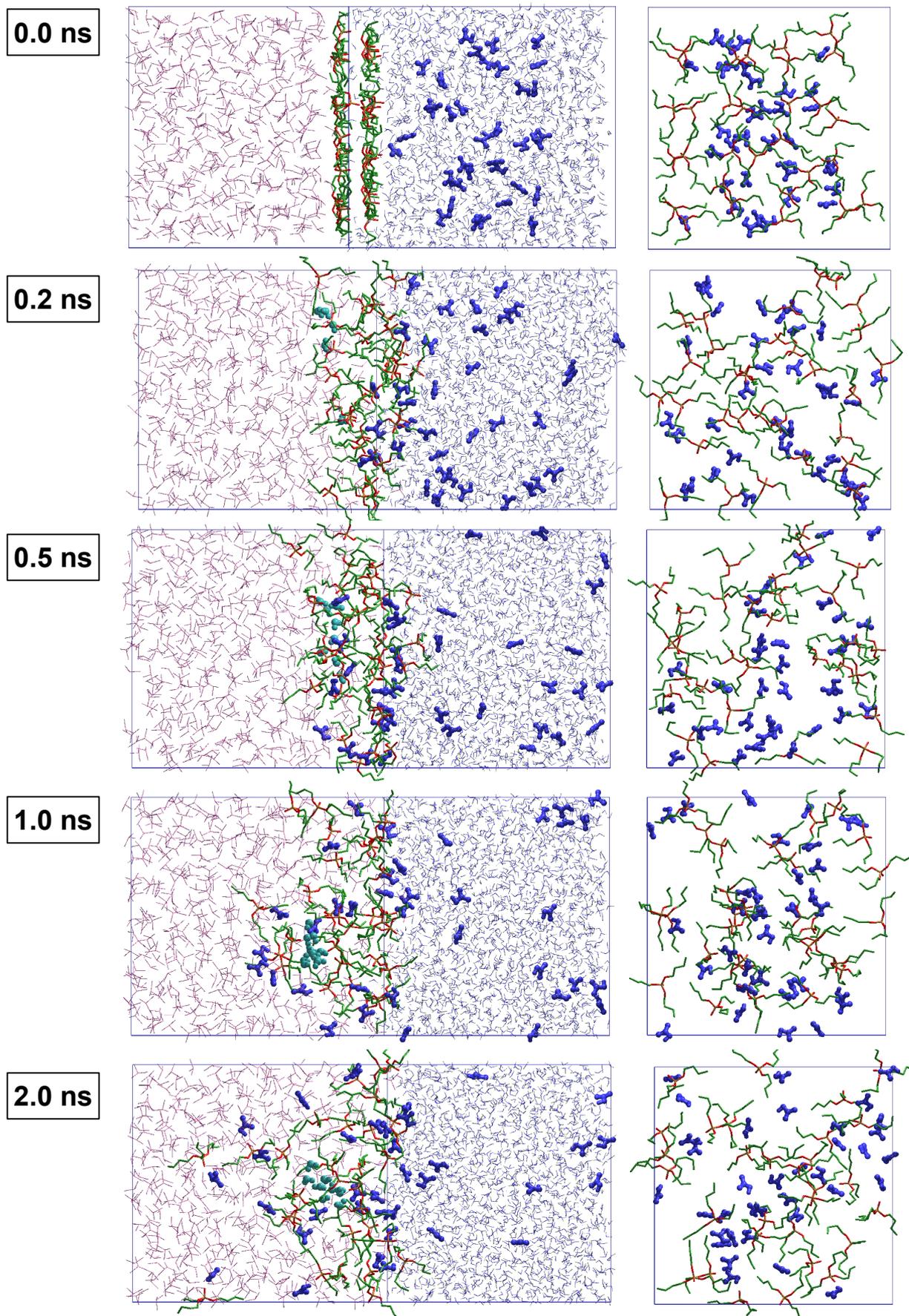


Figure 4-6: Orthogonal views of the acidic TBP<sub>30</sub> system B with 36 HNO<sub>3</sub> simulated at the water/chloroform interface. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

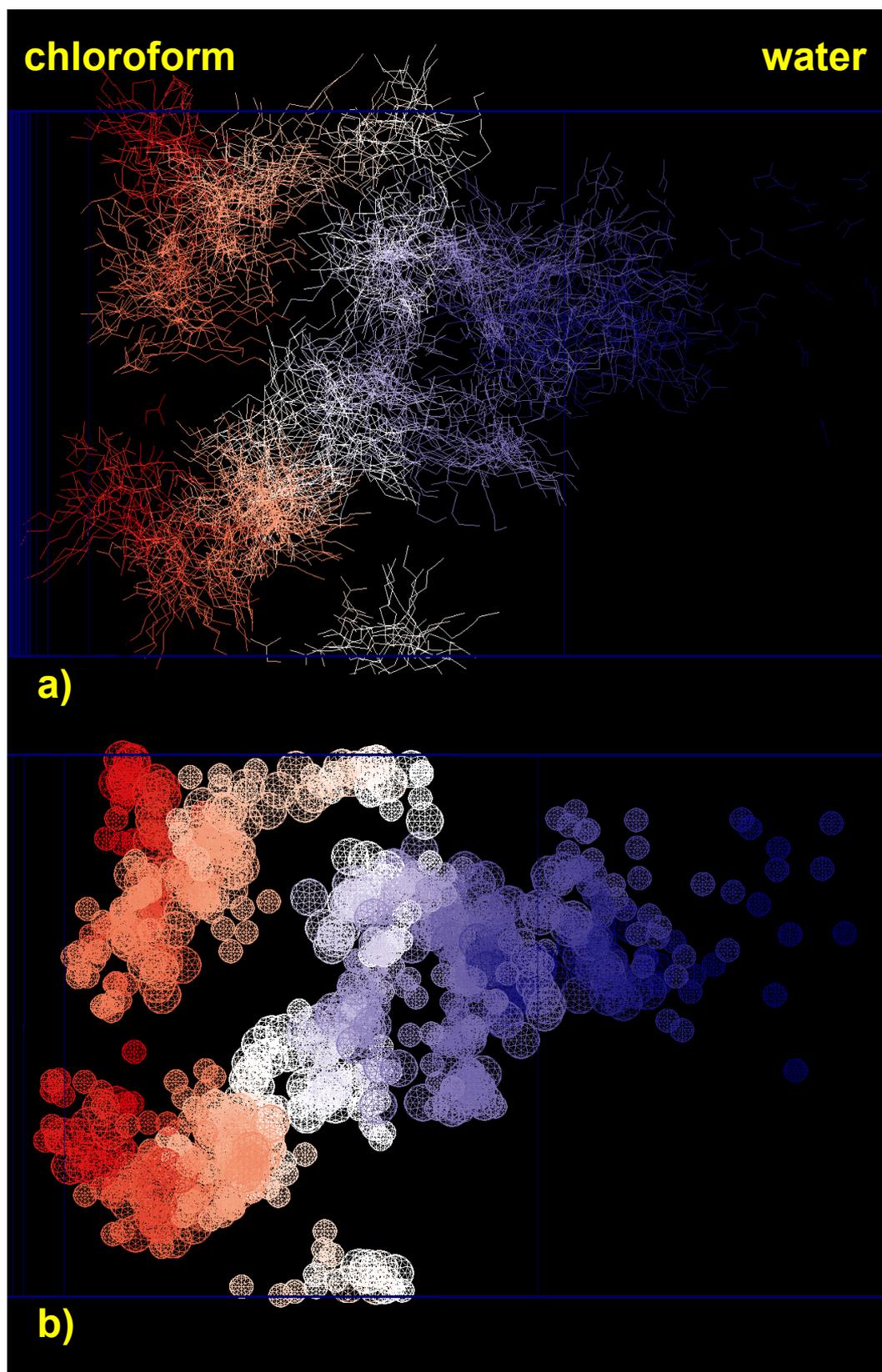


Figure 4-7: Cumulated views of the nitric acid extraction observed in system B between 0 ps (blue) and 2 ns (red) with a 10 ps time step. Only the two extracted TBP:HNO<sub>3</sub> complexes are shown, on top (a) as wireframe model, on the bottom (b) only the P and N atoms are shown. Other molecules are omitted for clarity.

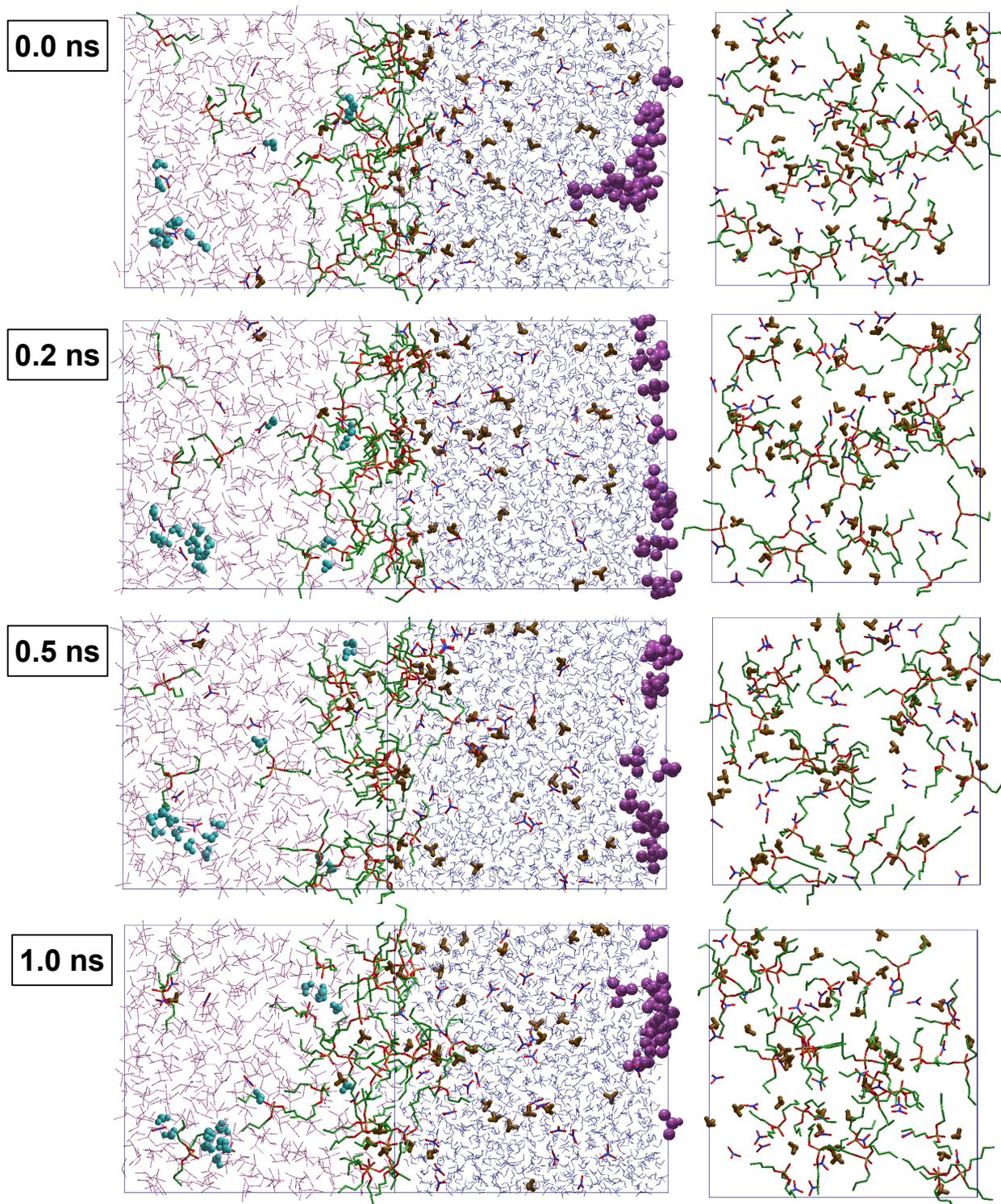


Figure 4-8: Orthogonal views of the acidic TBP<sub>30</sub> system C with 36 H<sub>3</sub>O<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated at the water/chloroform interface starting from the end of simulation B. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

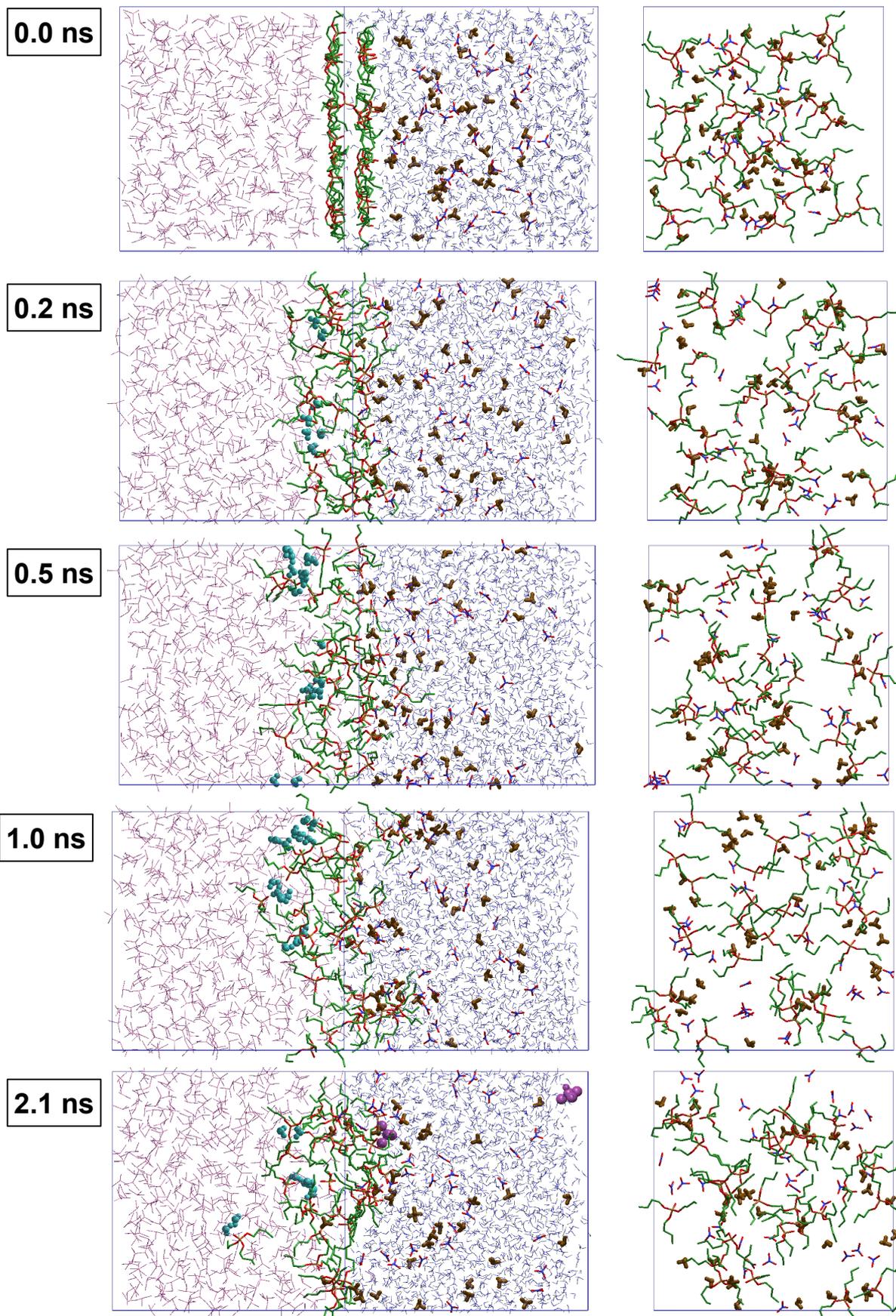


Figure 4-9: Orthogonal views of the acidic TBP<sub>30</sub> system C with 36 H<sub>3</sub>O<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated at the water/chloroform interface starting from a bilayer with P=O dipoles oriented towards the water phase. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

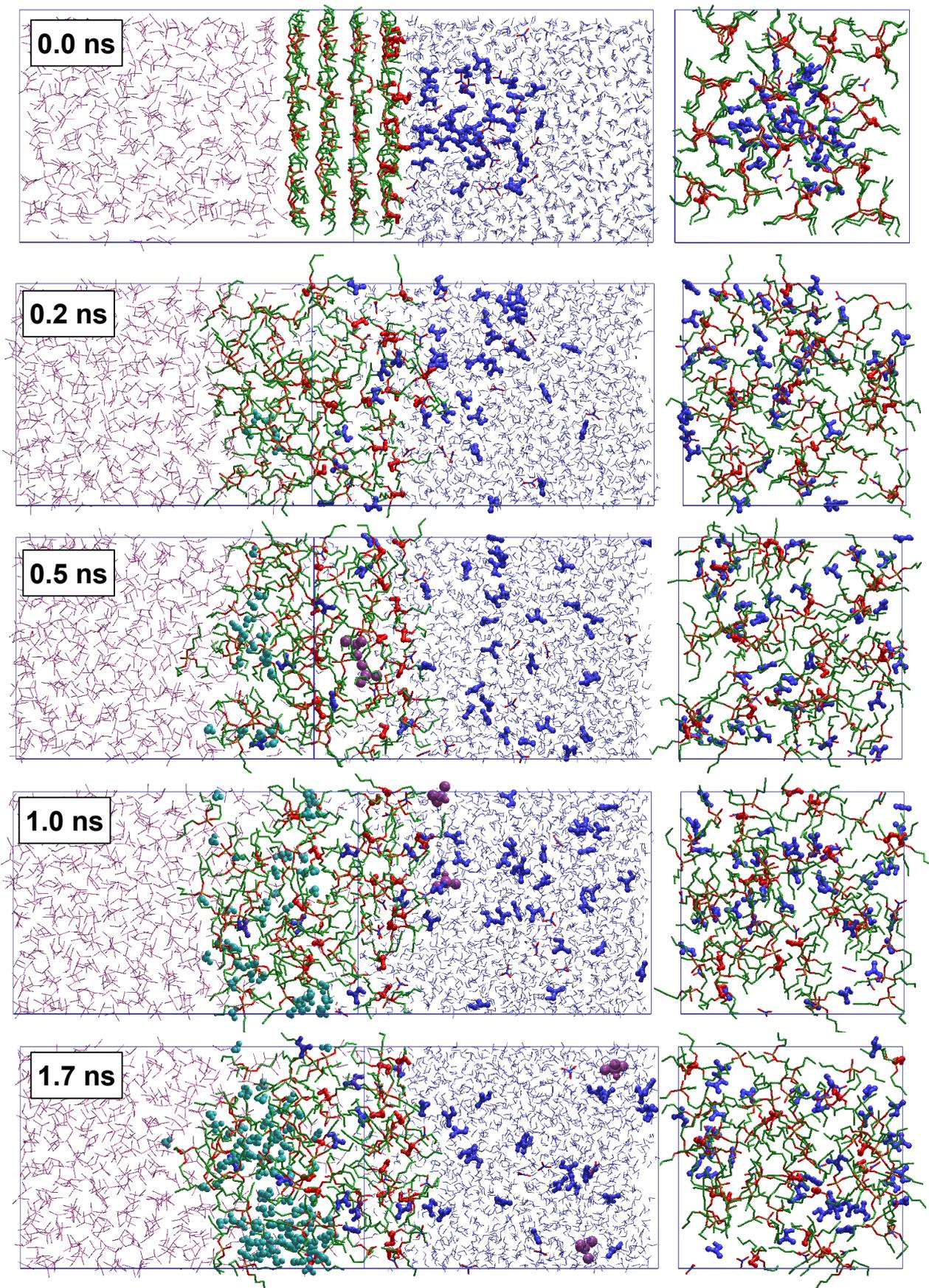


Figure 4-10: Orthogonal views of the acidic TBP<sub>30</sub> system E with 15 TBPH<sup>+</sup>NO<sub>3</sub><sup>-</sup> and 36 HNO<sub>3</sub> simulated at the water/chloroform interface. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

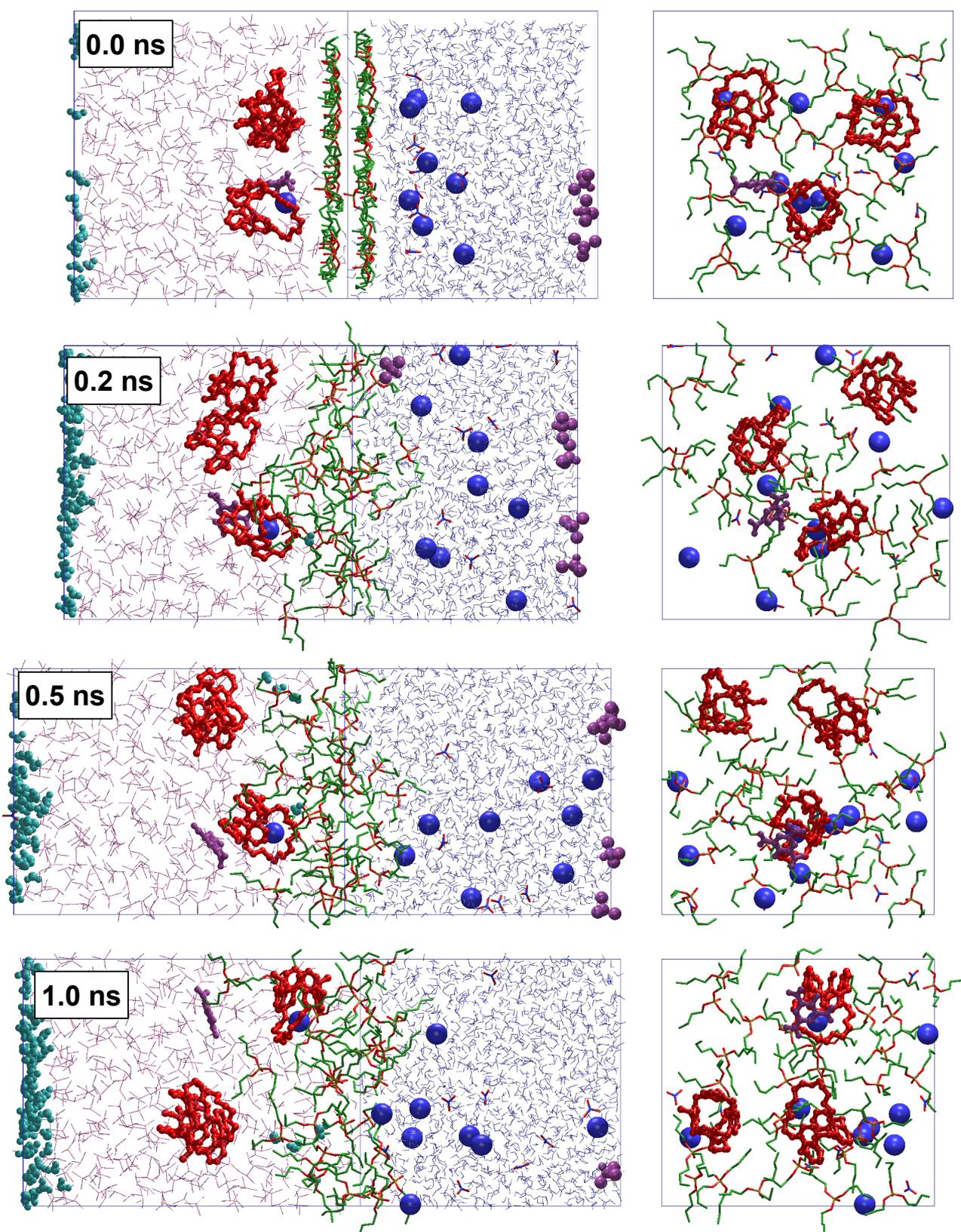


Figure 4-11: Orthogonal views of the TBP<sub>30</sub> system G with 2 L8, L8Cs<sup>+</sup>Pic<sup>-</sup> and 8 Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated at the water/chloroform interface. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

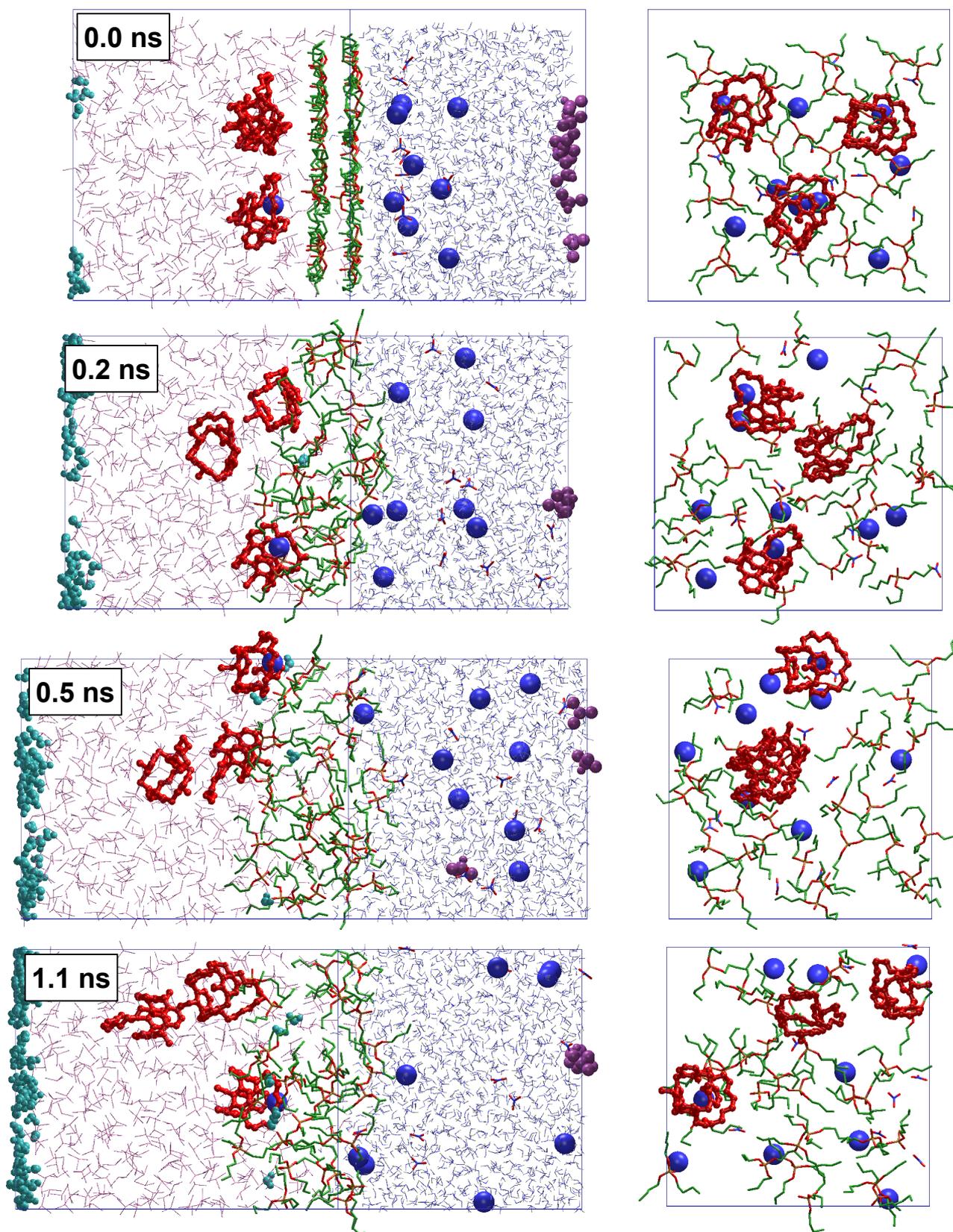


Figure 4-12: Orthogonal views of the TBP<sub>30</sub> system H with 2 L8, L8Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> and 8 Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated at the water/chloroform interface. Chloroform (water) molecules which are in water (chloroform) and which have their central atom more than 5 Å away from the interface are shown as a spacefilling model. Solvent molecules are omitted for clarity in the view perpendicular to the liquid-liquid interface.

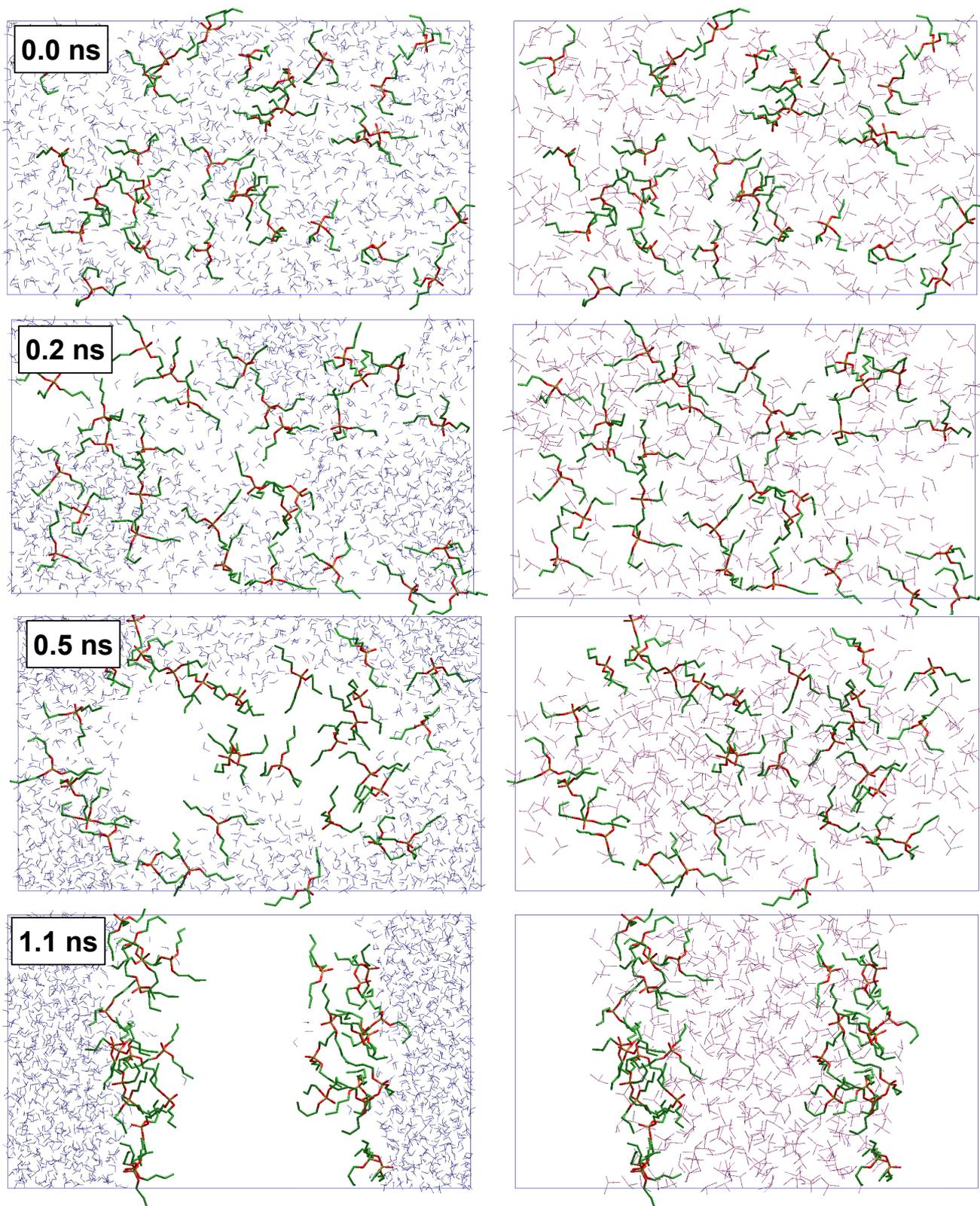


Figure 4-13: Phase separation of the "perfectly mixed" water / chloroform binary mixture, containing 30 TBP (system R4). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

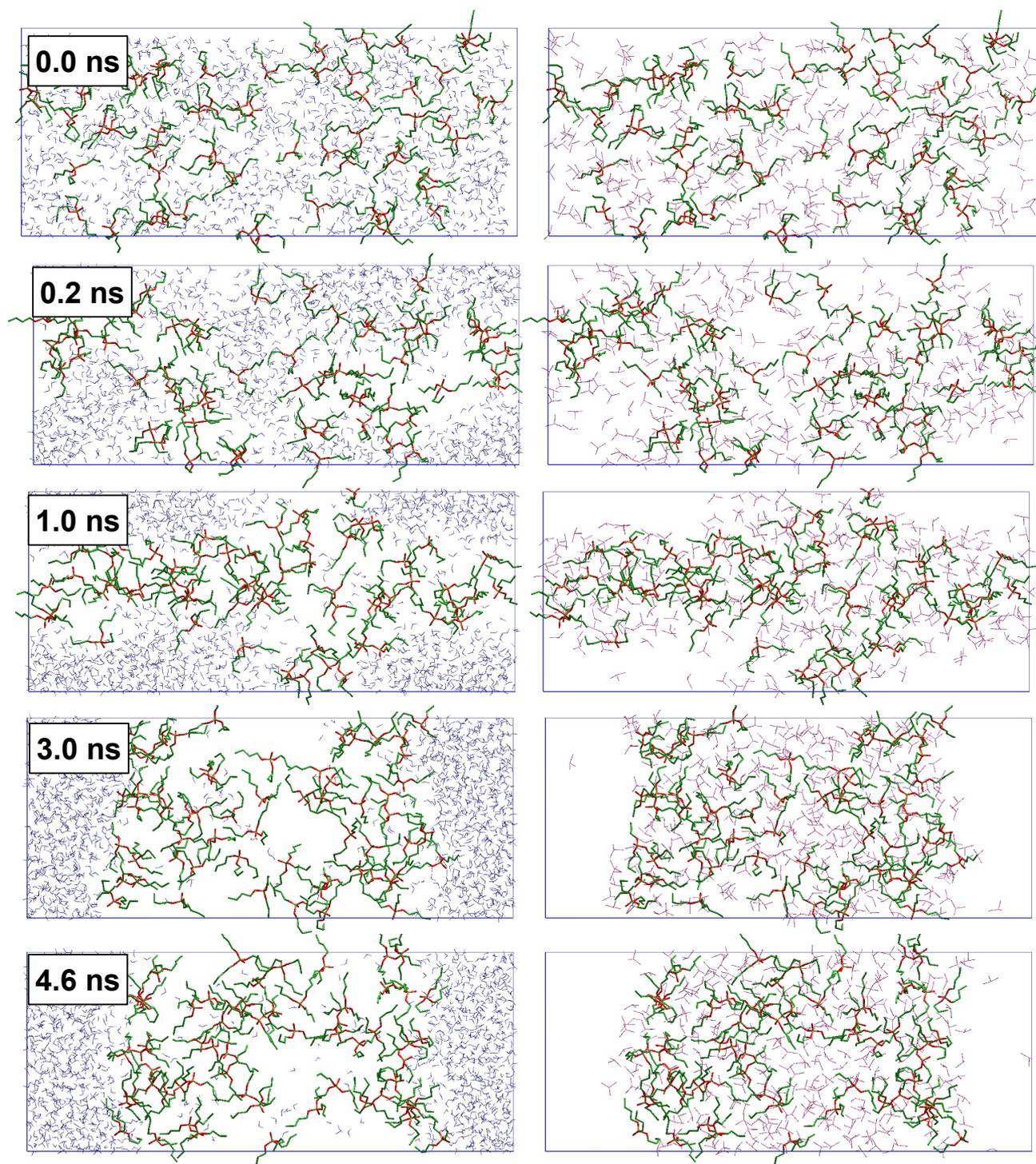


Figure 4-14: Demixing simulations of  $TBP_{60}$  simulated at the water/chloroform interface starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

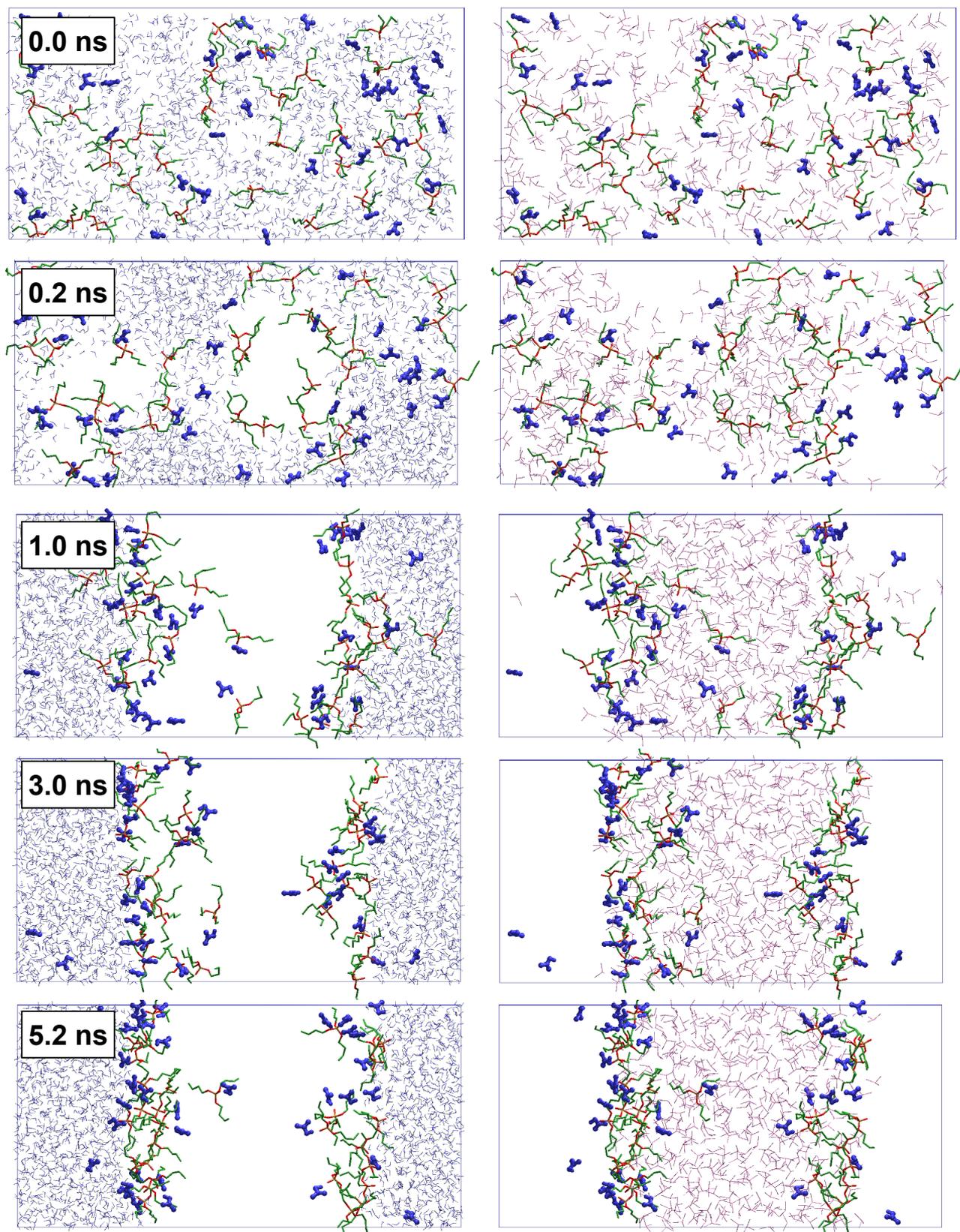


Figure 4-15: Phase separation of the "perfectly mixed" acidic water / chloroform binary mixture, containing 30 TBP and 36  $\text{HNO}_3$  (system B). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

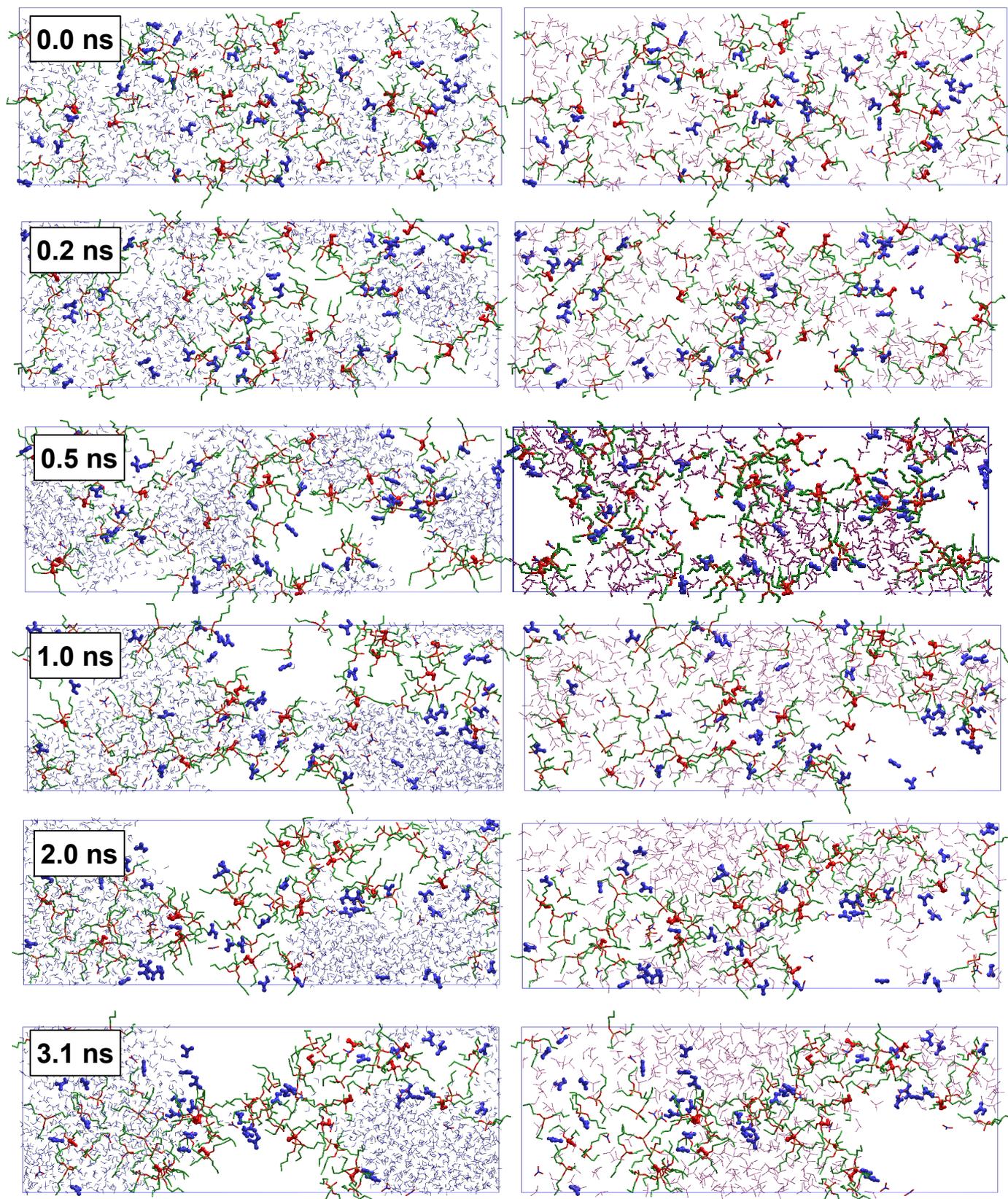


Figure 4-16: Demixing simulations of the acidic TBP<sub>30</sub> system E simulated at the water/chloroform interface starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

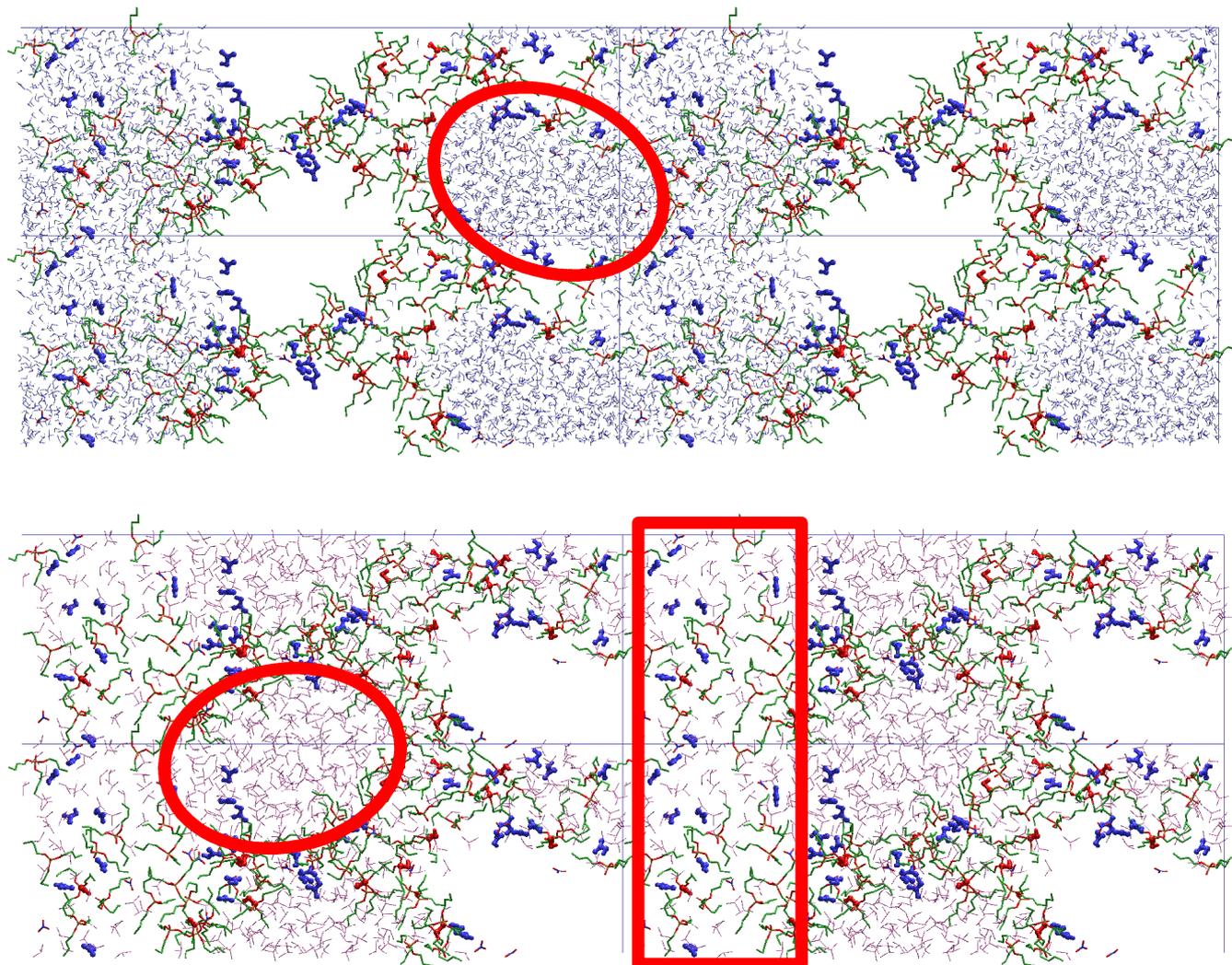


Figure 4-17: Pure and mixed solvent phases formed after 3 ns of demixing simulations of the acidic TBP/water/chloroform system E. On top a pure water bubble can be seen. Chloroform molecules are omitted for clarity. On the bottom a pure chloroform bubble and a mixed phase are indicated. Water molecules are omitted for clarity.

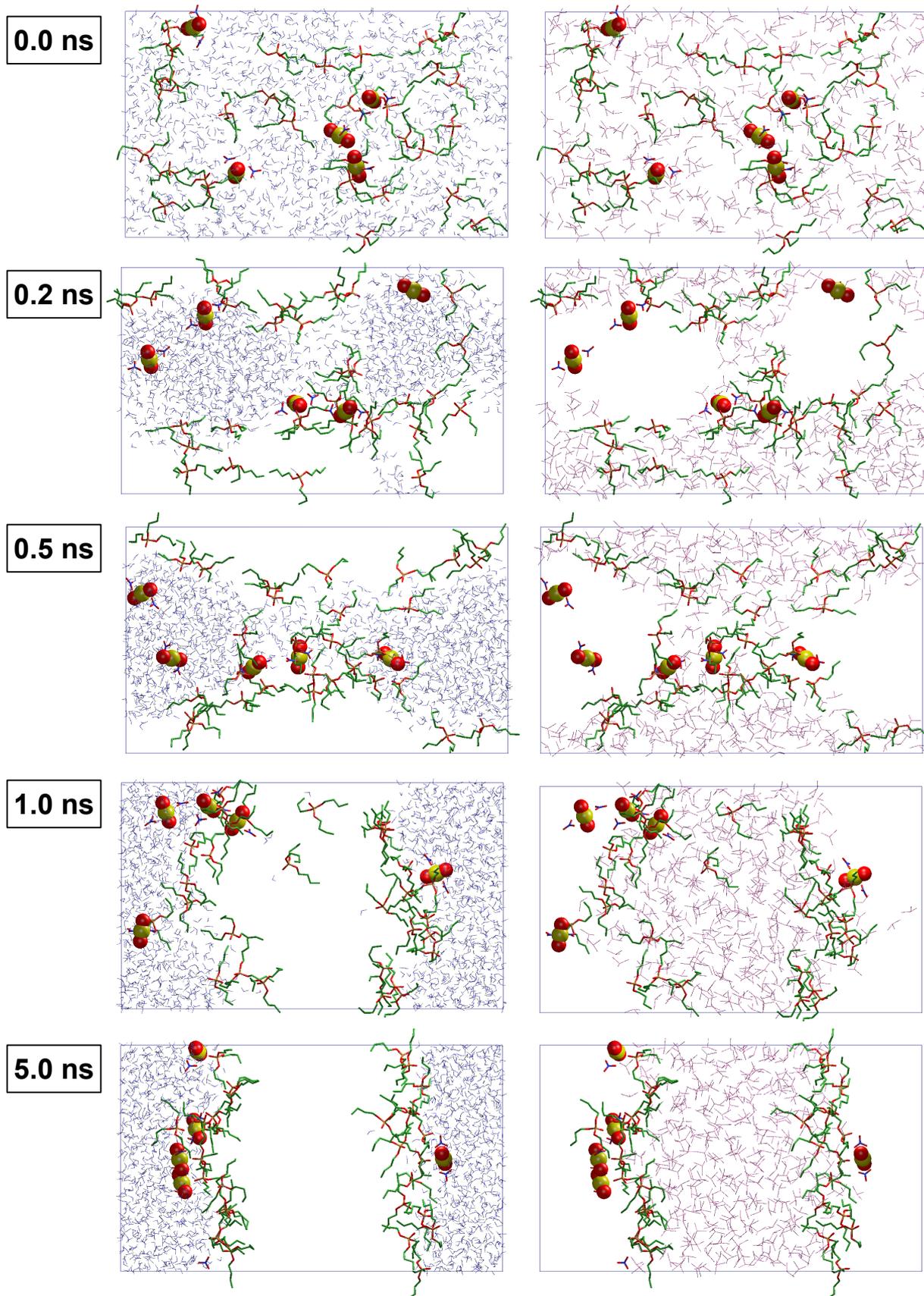


Figure 4-18: Phase separation of the "perfectly mixed" water / chloroform binary mixture, containing 30 TBP's and 5  $\text{UO}_2(\text{NO}_3)_2$  salts (system R5). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

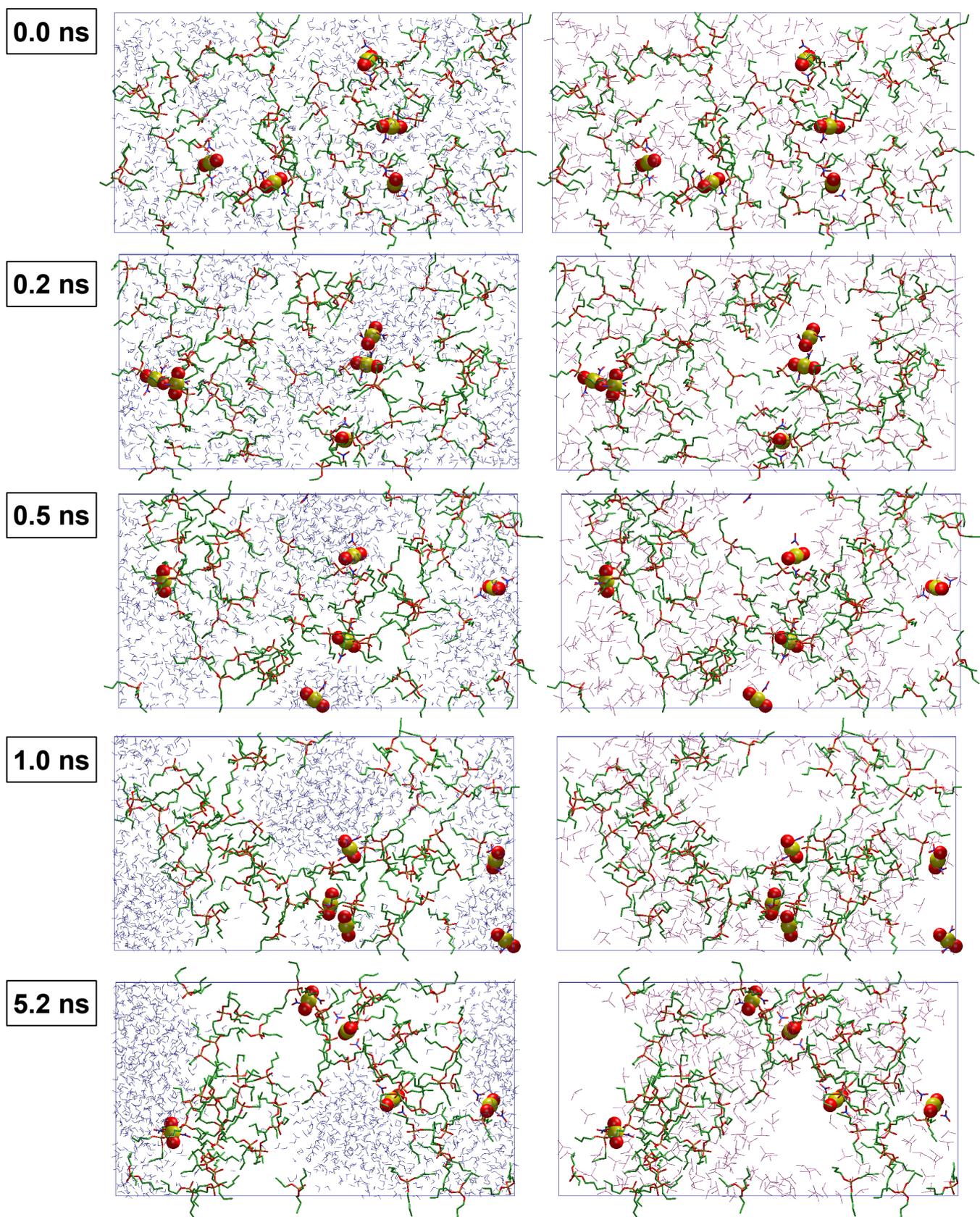


Figure 4-19: Demixing simulations of the TBP<sub>60</sub> system F with 5 uranyl salts simulated at the water/chloroform interface starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

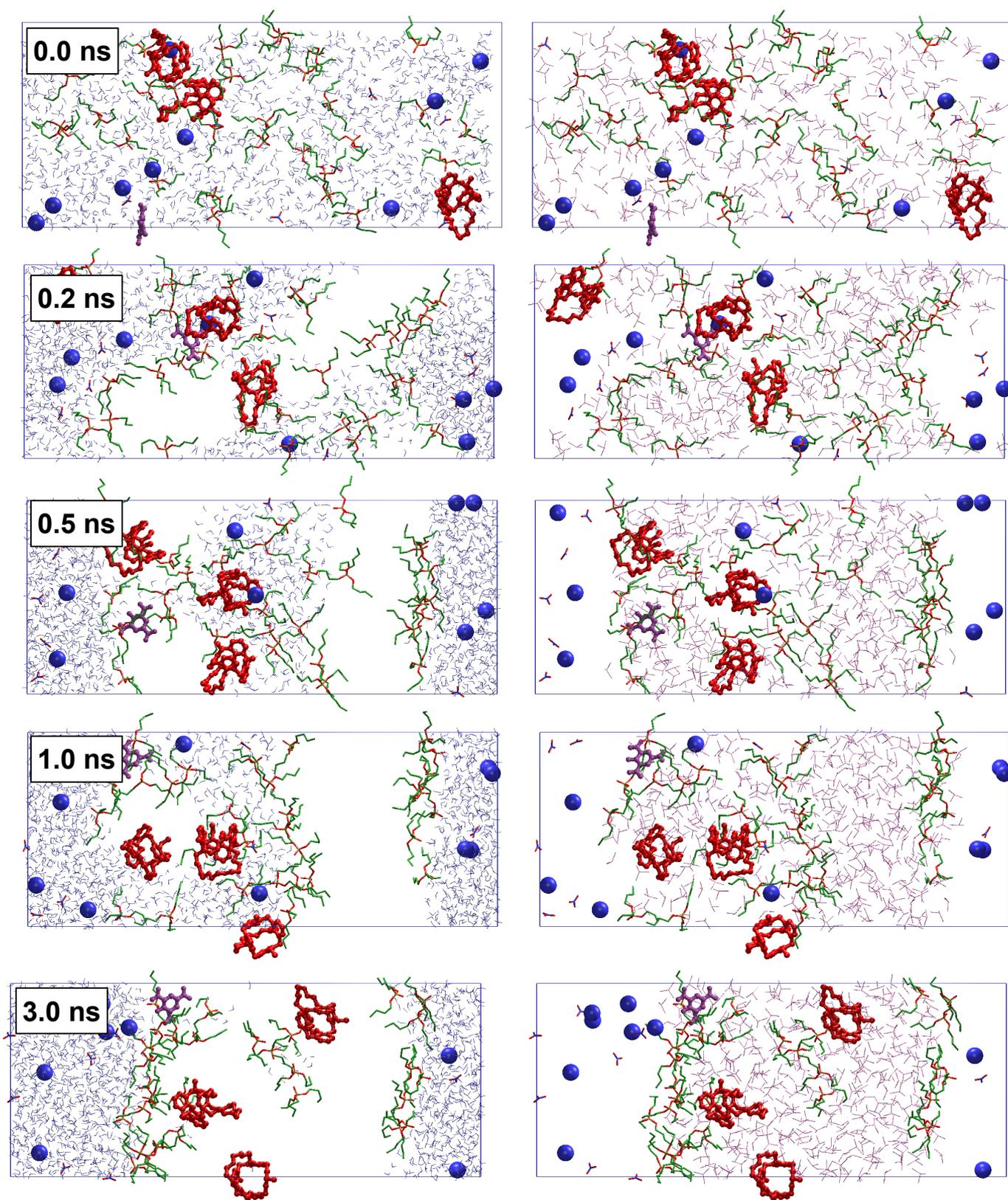


Figure 4-20: Demixing simulations of system G with 30 TBP, 2 L8, 1 L8Cs<sup>+</sup>Pic, 8 Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated in a rectangular water/chloroform box starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

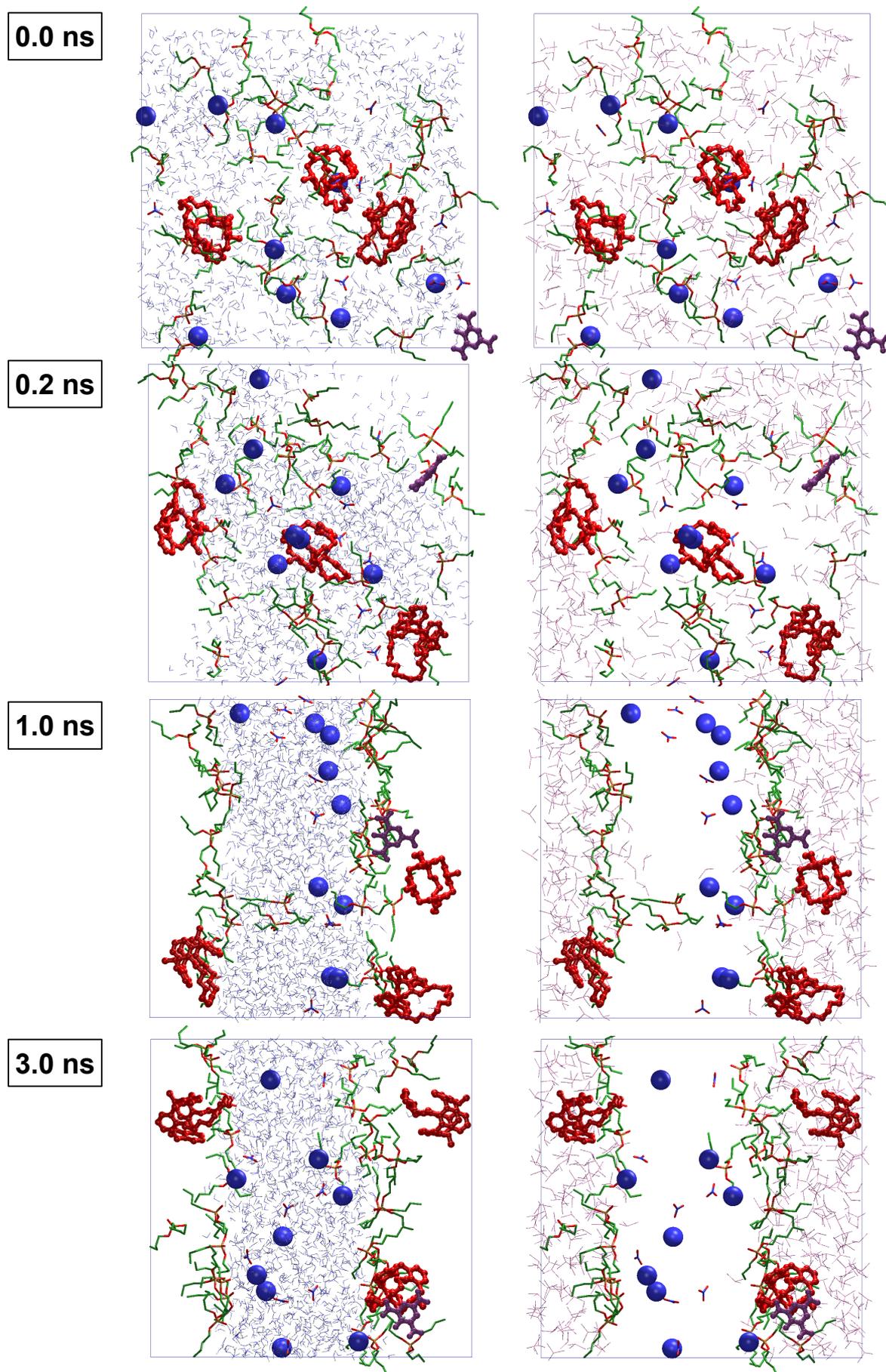


Figure 4-21: Demixing simulations of system G with 30 TBP, 2 L8, 1 L8Cs<sup>+</sup>Pic<sup>-</sup>, 8 Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated in a cubic water/chloroform box starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

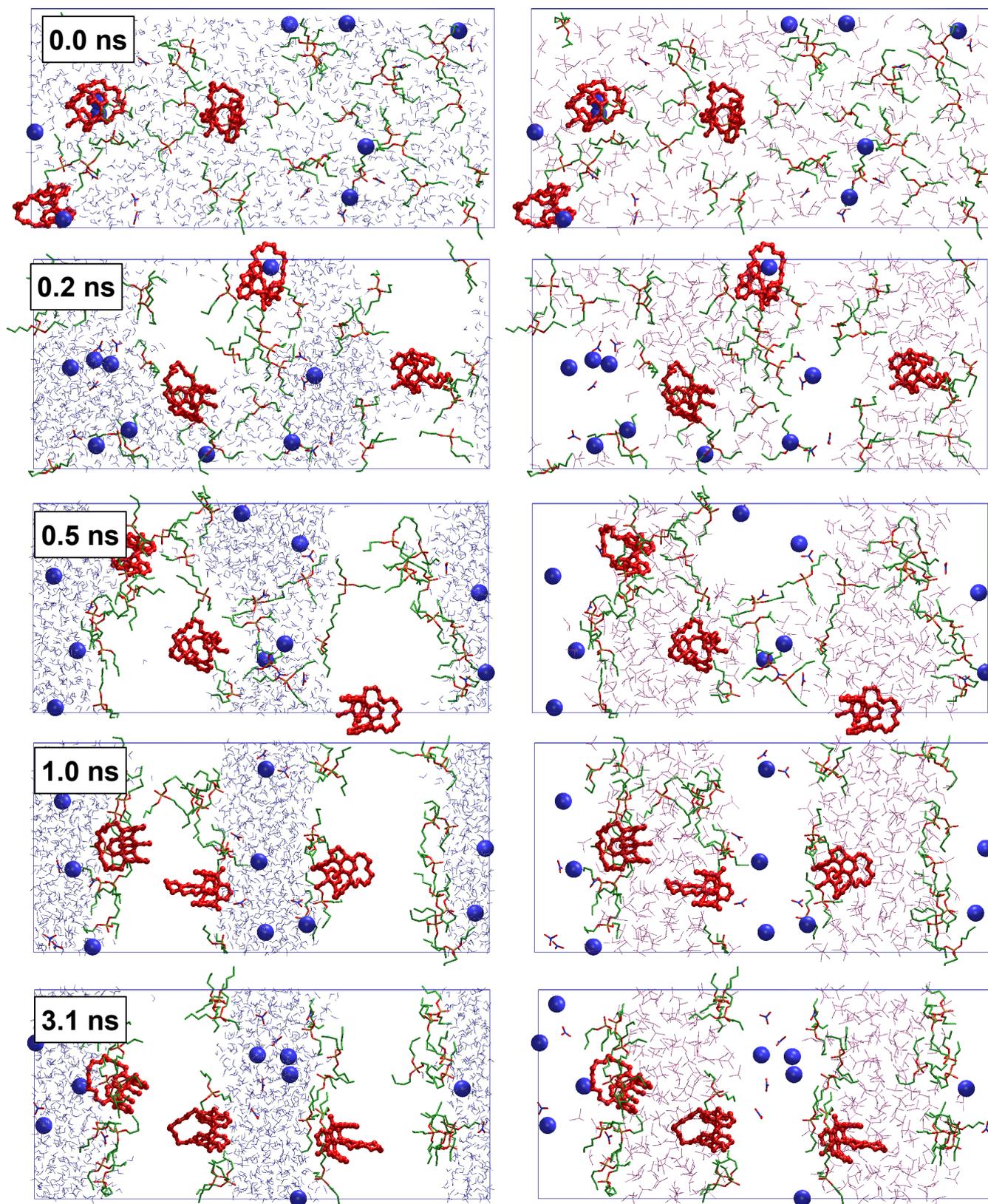


Figure 4-22: Demixing simulations of system H with 30 TBP, 2 L8, 1 L8Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup>, 8 Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated in a rectangular water/chloroform box starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

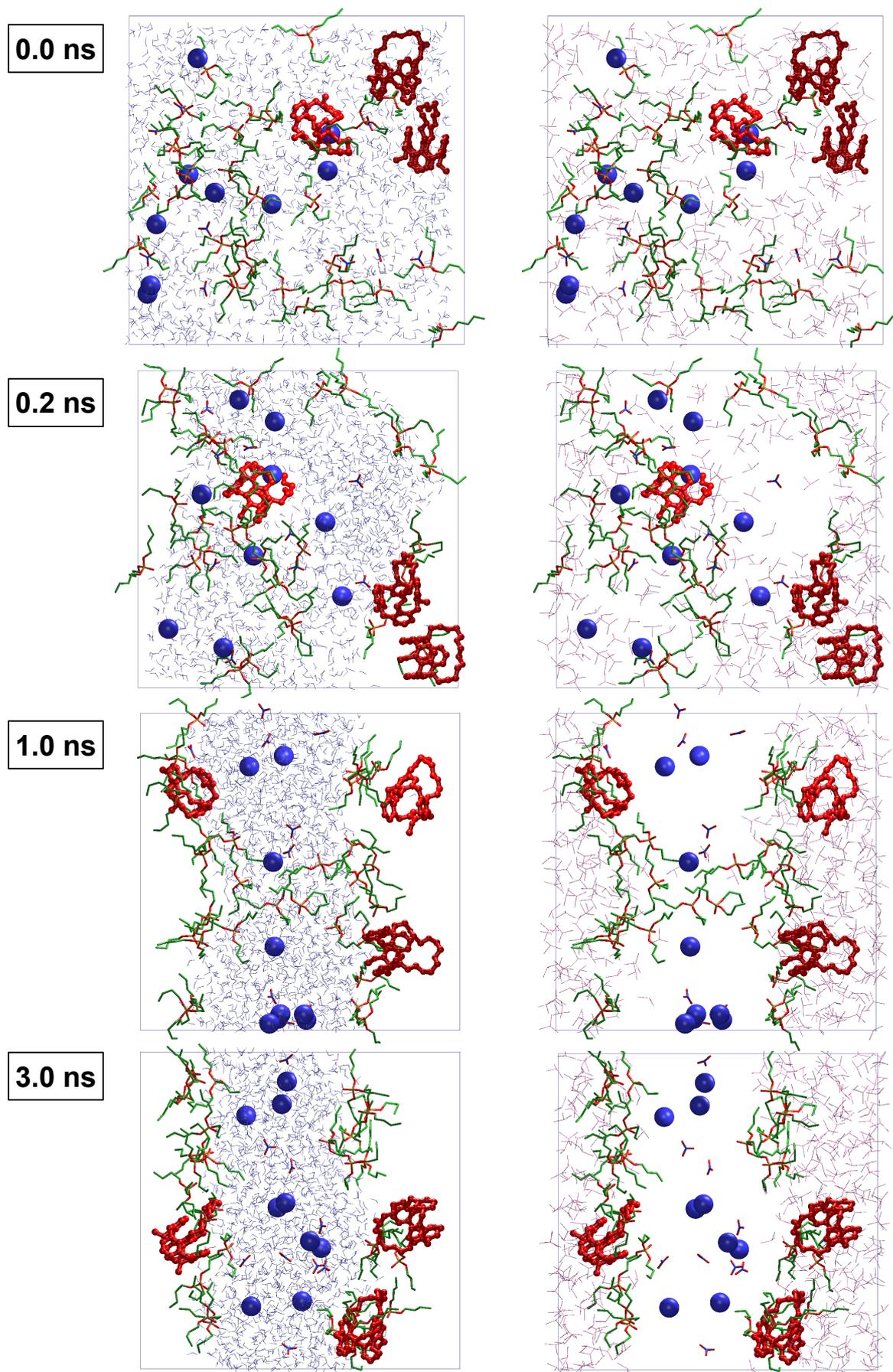


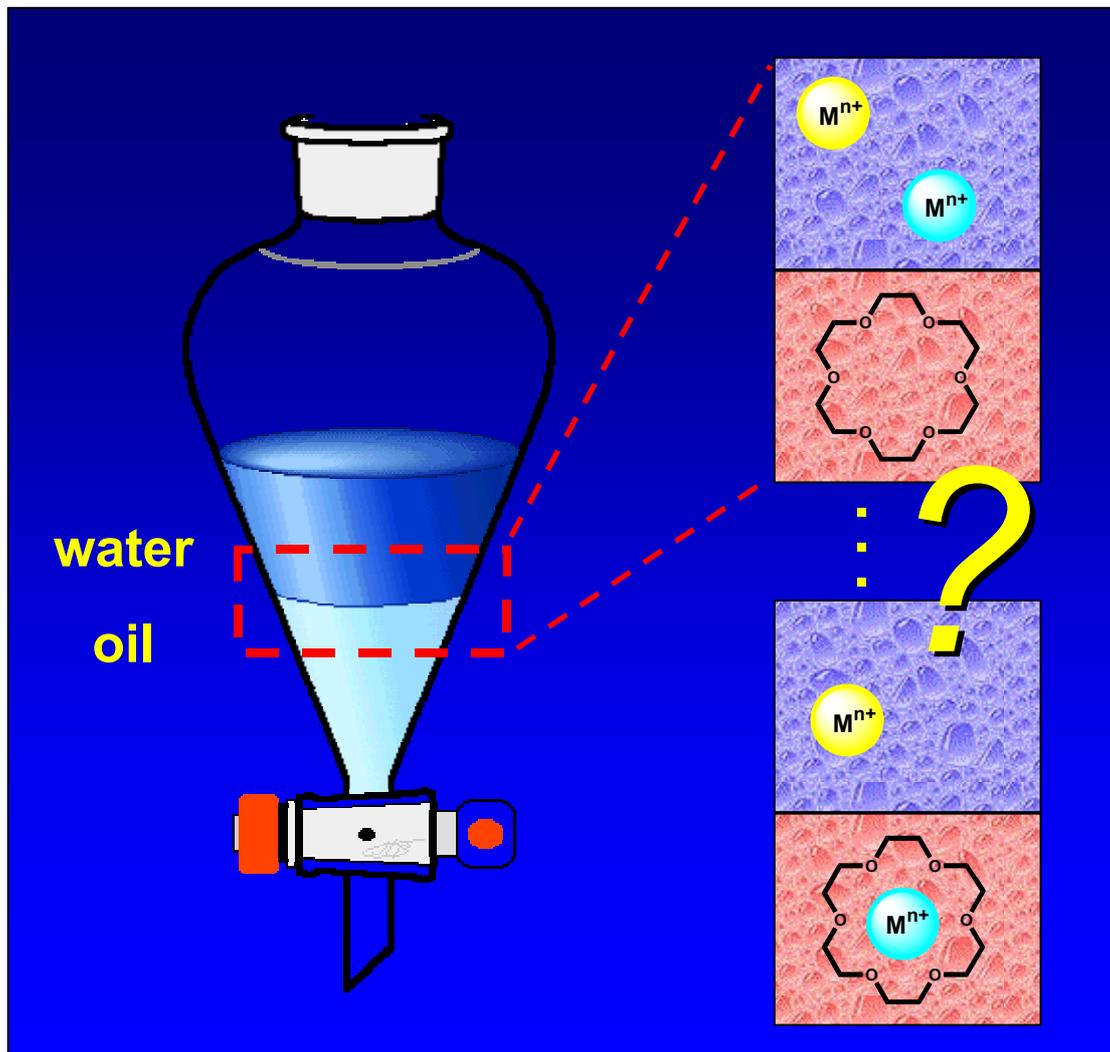
Figure 4-23: Demixing simulations of system **H** with 30 TBP, 2 L8, 1 L8Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup>, 8 Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> simulated in a cubic water/chloroform box starting from a completely mixed system (0 ns). For clarity, water (left column) and chloroform (right column) solvents are displayed separately instead of superposed.

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# Chapitre 5 × Chapter 5

Profils d'énergie libre de transfert à travers une interface  
dans des systèmes d'extraction liquide-liquide d'ions  
*Energy profiles for interface crossing  
in liquid-liquid ion extraction*

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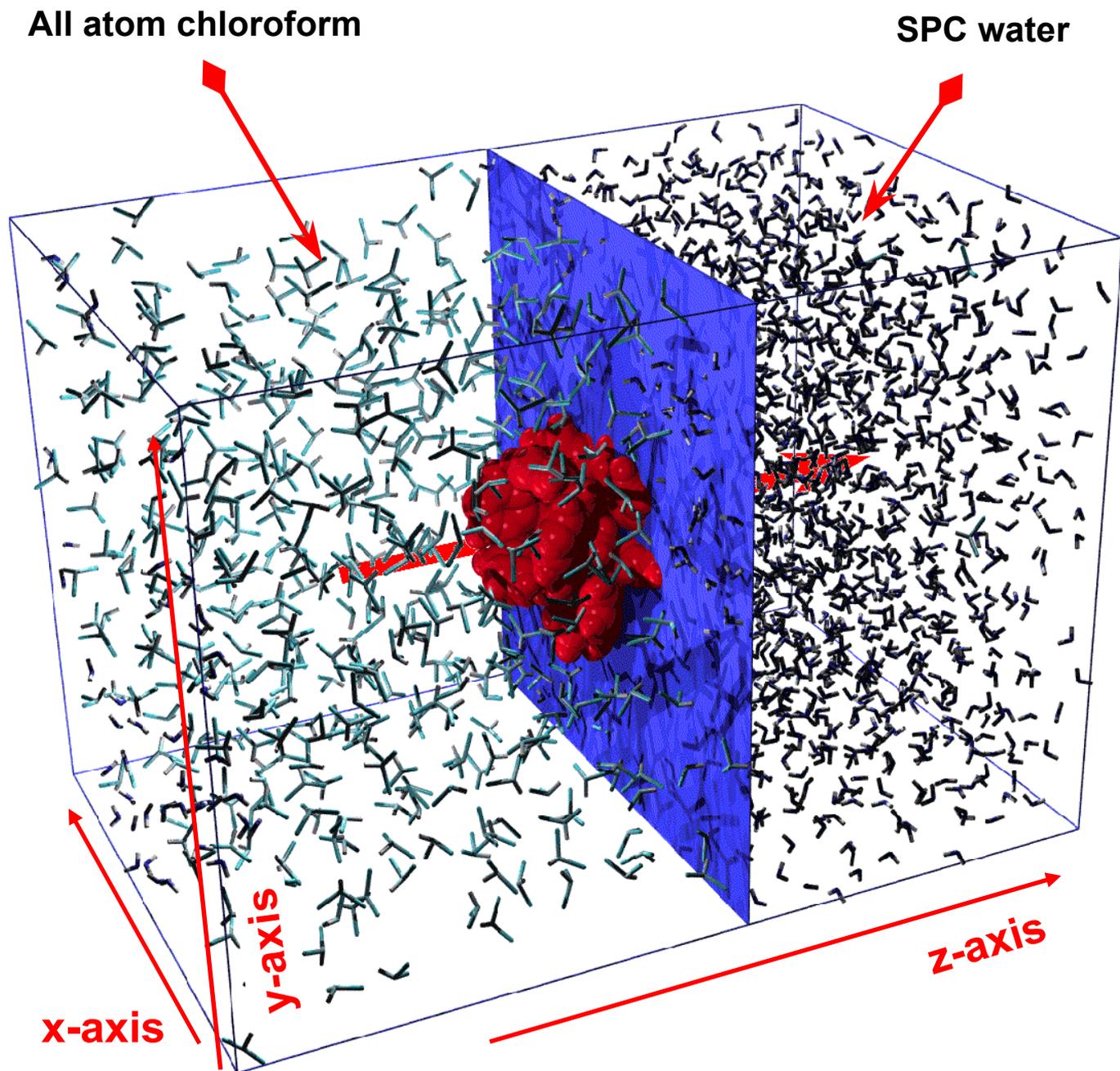


Figure 5-1: Definition of the reaction coordinate  $R$  along which the free energy profiles will be calculated. A bulky solute molecule is shown at the interface between both liquids.

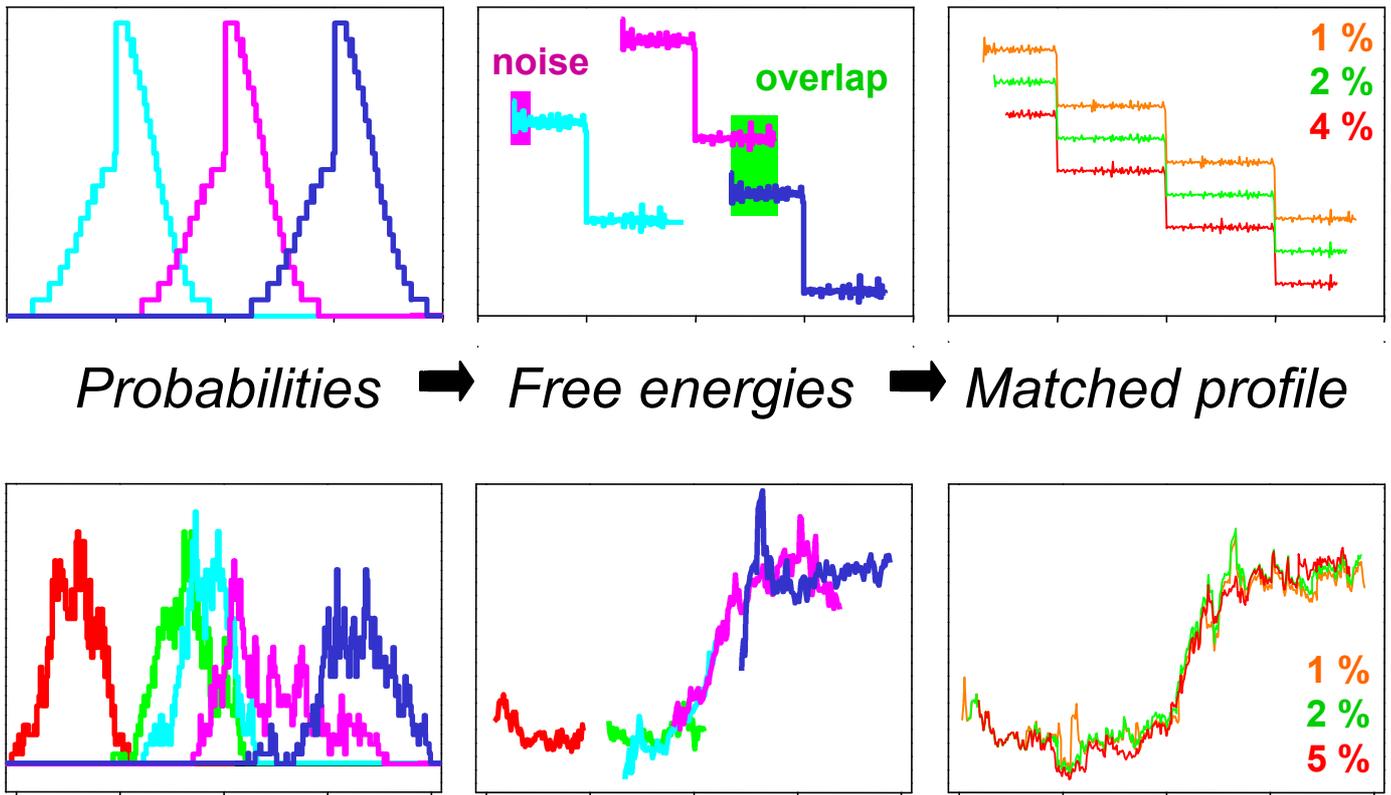


Figure 5-2: Schematic view of the matching of free energy profiles for simple step functions (on top) and for a "real" example with argon (on the bottom). A given percentage (as indicated) of the noisy tail regions was discarded from the free energy curves before matching in the overlap regions.

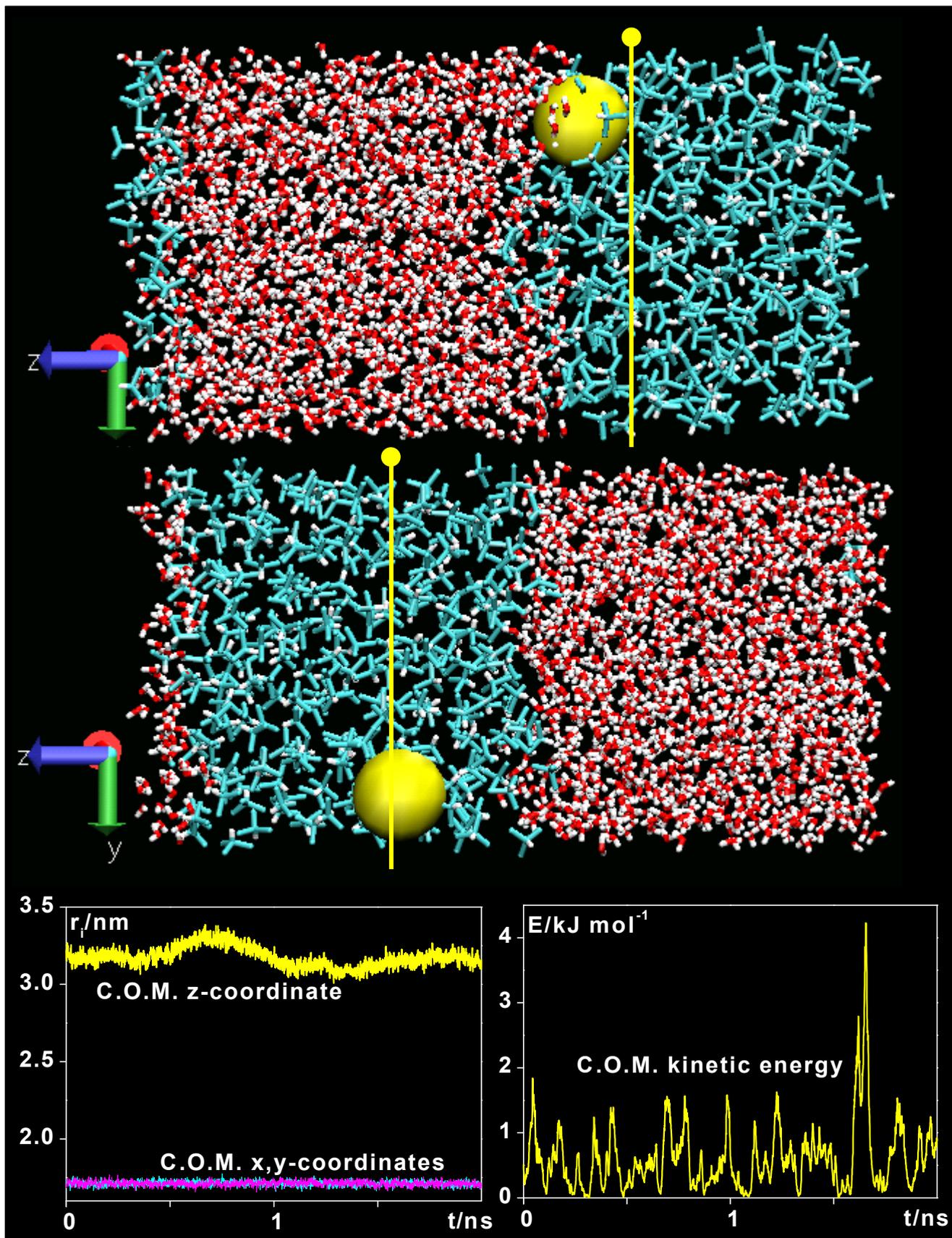


Figure 5-3: Center of mass (C.O.M.) motion leading to a solvent shift during the umbrella sampling runs. On top the argon was restrained to the chloroform side of the interface, below the reference position was moved to water. Due to C.O.M. motion the solvent has "followed" the solute and water/chloroform parts are inverted with respect to the above case. On the bottom, C.O.M. x-, y- and z-coordinates and C.O.M. kinetic energy are given as a function of simulation time.

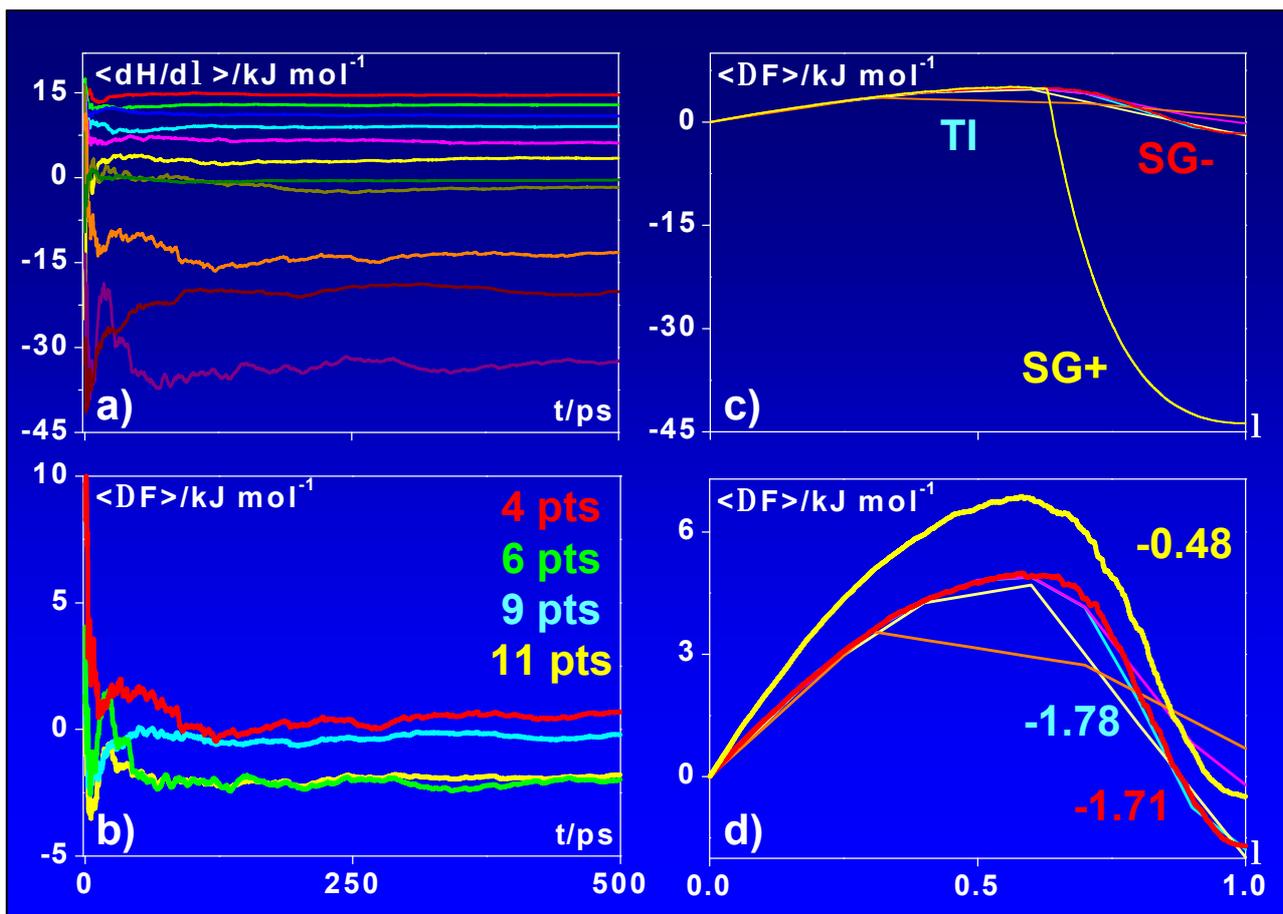


Figure 5-4: Appearing/disappearing of an argon atom in bulk chloroform solution using a slowgrowth (SG) and thermodynamic integration (TI) approach. a) Convergence of an 11-point TI as a function of simulation time. b) Running average of the free energy difference using 4, 6, 9 or 11 integration points. c, d) Superposition of TI and SG appearing (SG+) / disappearing (SG-) with position restraining (c) or without (d).

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# Supplementary material

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## Note

A CD-ROM is included in the back-cover of this thesis, volume 2. It contains supplementary material related to the present manuscript, like for instance electronic versions of articles that were published, where available.

The contents of the CD should be accessible from a great variety of computer platforms and operating systems such as Linux, Unix, Windows or Macintosh computers. Most files are in "Portable Document Format" (PDF). The file "index.pdf" in the root directory should be used as a starting point.